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# Canadian Journal of Chemistry

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## THE PHOTOLYSIS OF DIMETHYL MERCURY IN HEXANE SOLUTION AT LOW TEMPERATURES<sup>1</sup>

BY D. H. DERBYSHIRE<sup>2</sup> AND E. W. R. STEACIE

### ABSTRACT

The photolysis of dimethyl mercury in solution in *n*-hexane has been studied over the temperature range +25° C. to -80° C. The results indicate that methane is produced by an abstraction reaction involving the solvent, and ethane is produced by dimerization of methyl radicals. The mechanism of the reaction is discussed, and it is concluded that the abstraction reaction involves radicals possessing considerable energy carried over from the photodissociation.

### INTRODUCTION

A considerable number of investigations of the photolysis of mercury dimethyl have been made. The indications are that at higher temperatures "hot" radical effects are of no importance (2, 11). At room temperature, however, there are indications that such effects are becoming noticeable (7). There are also indications of such effects in other systems at low temperatures (7, 8, 13, 14, 15, 17) and in the liquid state. It therefore seemed of interest to investigate the mercury dimethyl photolysis at low temperatures in solution. *n*-Hexane was used as a solvent because of its ready availability in a pure state, its low melting point, and its ease of manipulation in a vacuum apparatus.

### EXPERIMENTAL

#### Materials

Dimethyl mercury as supplied by Messrs. H. K. Lights Ltd. was dried over anhydrous calcium chloride and purified by a bulb to bulb distillation; only the middle fraction was collected. The compound was thoroughly degassed and was stored in the dark in a glass bulb isolated by a mercury cutoff. The vapor pressures agreed with the values recorded by Linnett and Thompson (6). The compound was degassed further before each experiment.

The *n*-hexane was a "Phillips Pure Hydrocarbon" stated to be 99 mole % pure. It was found, however, that in 1 cm. depths the material absorbed *ca.*

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70% of incident light in the region of 2300 Å; a region where pure hexane is transparent. It was purified by passing through a column of silica gel (3) which removed practically all of the light absorbing impurities. The product obtained transmitted 99% of incident light at 2300 Å in 1 cm. depths. The hexane was dried over anhydrous calcium chloride and purified by a bulb to bulb distillation, the middle fraction being collected. Since relatively large quantities of hexane were used (*ca.* 1 ml. of liquid in each experiment), about 100 ml. were stored in a reservoir containing a "cold finger" isolated by a mercury cutoff. The hydrocarbon was degassed by filling the cold finger with a freezing mixture at  $-80^{\circ}\text{C}$ . and pumping continuously for several hours while allowing the hexane to reflux.

#### *Light Source*

Preliminary experiments using the unfiltered radiation from a low pressure mercury lamp showed that mercury dimethyl in hexane solution was photolyzed at a convenient rate at room temperature and that metallic mercury was deposited.

Reichardt and Bonhoeffer (12) have shown that hexane is capable of dissolving a significant amount of mercury and that the saturated solutions so obtained absorb a considerable fraction of incident light in the region 2530–2650 Å. Phibbs and Darwent (9) have also shown that such solutions undergo a photosensitized decomposition when irradiated with mercury resonance radiation. In order to avoid complicating factors due to a concomitant mercury photosensitized reaction, a light source was therefore used having a negligible intensity in the region of 2537 Å. Owing to the broadening of the mercury resonance line in solution, a high pressure mercury arc emitting a reversed line at 2537 Å is obviously unsuitable.

The light source finally adopted was a cadmium–neon discharge lamp, which had strong lines at 2288 Å and 3261 Å with only weak lines in between (10). The lamp was enclosed in a furnace with a small additional heater situated near the center of the lamp. With this arrangement the central part of the lamp could be maintained about  $15^{\circ}$  higher than the two electrodes, thus preventing the distillation of cadmium to the center of the tube and so the obscuring of the window. The lamp was operated at about  $280^{\circ}\text{C}$ . with a current of 80 ma. from a Jefferson sign transformer. The radiation from the lamp was roughly collimated by passing through a 5 cm. quartz cell containing distilled water which also served to absorb infrared radiation. Spectrographic investigation showed that the cadmium line at 2288 Å was almost completely absorbed by the solutions of dimethyl mercury in hexane, but the 3261 Å line was relatively unaffected; the unfiltered cadmium radiation was therefore used as a light source. The light intensity was varied by means of neutral density filters consisting of chromel deposited on quartz.

#### *Apparatus*

The analytical method was designed to handle samples of liquid of about 1 ml. and so the photolyses were carried out in a quartz cell of approximately 5 cm. diameter and 0.05 cm. in depth. The cell was provided with two outlets



so that after filling, it could be sealed off and removed to carry out the photolysis, after which it was resealed into the apparatus and the products liberated into the analytical apparatus by breaking a thin glass internal seal with a plunger. The solutions used contained about 1 mole % of dimethyl mercury and never more than 5% of the dimethyl mercury was decomposed during the photolysis.

Solutions were prepared by taking known volumes of dimethyl mercury vapor at a given temperature and pressure and mixing them with a fixed quantity of liquid hexane (measured at  $-78^{\circ}\text{C}.$ ), after which the reagents were condensed into the cell and the apparatus sealed off at a constriction. Mercury cutoffs were used at all points in the apparatus which came into more than fleeting contact with the vapor of hexane and dimethyl mercury.

The gaseous products of the reaction were found to be methane and ethane in a ratio of about 4:1 in the experiments at  $25^{\circ}\text{C}.$  The quantities of these gases produced were, however, quite small, e.g. about 0.1 ml. of methane and 0.025 ml. of ethane measured at N.T.P., and an analytical method had to be devised for separating these small quantities of methane and ethane from the large liquid residue. It was found convenient to divide the analytical procedure into two stages, the first being the separation of methane and ethane from the liquid residue, and the second the resolution of the mixture of methane and ethane.

After an experiment the contents of the cell were distilled into a column at the top of which was a "cold finger" maintained at  $-78^{\circ}\text{C}.$  with a freezing mixture. The liquid was refluxed continuously in this vessel while the degassing was carried out. The combined pressure of methane and ethane above the solution was measured by a McLeod gauge, but since hexane has a vapor pressure of *ca.* 0.1 mm. at  $-78^{\circ}\text{C}.$ , it was necessary to insert a trap maintained at  $-160^{\circ}\text{C}.$  between the refluxing liquid and the McLeod gauge in order to remove the hexane vapor from the methane and ethane. The two gases were then pumped away by a Toepler pump until the total pressure above the liquid residue was reduced to  $10^{-3}$  mm. and remained stationary at this value. Experiments in which known quantities of methane and ethane were taken and mixed with hexane showed that by this procedure these gases could be removed from hexane solution practically completely. With quantities of gases of the order found in the photolysis experiments the reproducibility was of the order 3-4%.

The mixtures of methane and ethane were separated by low temperature fractionation using a modified type of Ward still (5). Mass spectrometer analyses of the products showed no traces of hexane.

#### *Liquid Residue*

In a number of experiments the infrared spectra of the liquid contents of the cell were determined before and after irradiation, using a Perkin-Elmer double-beam spectrometer. These were identical in the region of  $900\text{ cm.}^{-1}$  showing that detectable amounts of unsaturated hydrocarbons were not produced in the reaction. However, it would appear from the values of the extinction

coefficients for ethylenic hydrocarbons quoted in the literature (1) that this method may be insufficiently sensitive to detect the amounts of unsaturated hydrocarbon expected.

#### *Low Temperature Photolysis*

For the irradiations at low temperatures, several types of apparatus were constructed and used with varying degrees of success.

The first type of apparatus constructed was similar in principle to apparatus used in low-temperature calorimetric work. The thermostat consisted of an aluminum block suspended in a steel cylinder from a cup which also formed part of the lid. The apparatus was evacuated and light entered the apparatus through quartz windows sealed into the sides of the cylinder. The aluminum block was cooled by placing a refrigerant, e.g., liquid nitrogen or carbon dioxide - acetone, in the steel cup, and the temperature brought to a constant value by balancing the loss of heat from the block by a heater in good thermal contact with the aluminum block. By varying the current in the heater and the thermal contact between the block and the cup containing the refrigerant, the temperature of the block could be varied over a wide range. The cell was placed in a slot cut into the side of the aluminum block and light entered the cell through a circular aperture cut into the face of the thermostat. Thermal contact with the block was made at the back and sides of the cell. This type of apparatus was convenient to use and experiments were conducted with the thermostat at temperatures down to  $-70^{\circ}\text{C}$ . It was found, however, that the thermal contact between cell and thermostat was not sufficient and considerable temperature gradients existed between the cell and the aluminum block. In view of this fact, extensive experiments with this type of system were not carried out at low temperatures but the apparatus was used for experiments in the vicinity of room temperature.

The apparatus finally adopted for the low temperature experiments was of a more conventional type and consisted essentially of an unsilvered glass dewar filled with ethyl alcohol. Light was conducted into the cell through quartz windows of approximately 3 cm. diameter sealed into the sides of the dewar. The alcohol used as a bath liquid was purified by the method of Leighton (4) and had a transmission of 80% at  $2288\text{ \AA}$  in 1 cm. depths. The cell was placed 1 mm. or less behind the quartz window and so absorption of light by the alcohol was negligible. The cooling of the bath liquid was carried out by placing a "cold finger" into the alcohol. The "cold finger" consisted of a glass cylinder closed at one end, with numerous indentations to increase the surface area and containing a refrigerant such as carbon dioxide - acetone. The glass cylinder was sealed into the bottom of a long silvered glass dewar which formed a reservoir which could be filled with solid carbon dioxide. With a carbon dioxide - acetone mixture in the "cold finger", the bath could be maintained at  $-60^{\circ} \pm 0.5^{\circ}\text{C}$ . For temperatures between  $-60^{\circ}\text{C}$ . and  $0^{\circ}\text{C}$ . heat was supplied to the thermostat by a heater of chromel wire wound around the "cold finger". This type of thermostat was found to be extremely convenient for the low temperature experiments.

## RESULTS

Mixtures of hexane and dimethyl mercury were found to be quite stable when kept in the dark at 25° C. Irradiation of liquid hexane in the presence of mercury produced no gaseous products.

TABLE I  
Temperature = 25° C.;  $\text{Hg}(\text{CH}_3)_2 = \text{ca. } 10^{-4}$  mole;  $\text{C}_6\text{H}_{14} = \text{ca. } 10^{-2}$  mole

Duration of run in hours	6	12	12	12	18	24
$\text{CH}_4$ produced, ml. (N.T.P.)/hr. $\times 10^{-3}$	7.0	7.0	6.9	6.9	6.8	6.9
$\text{C}_2\text{H}_6$ produced, " " "	1.6	1.6	1.5	1.6	1.6	1.6

The results given in Table I show that the rate of production of methane and ethane at 25° C. is independent of time, and that there is no induction period associated with the reaction. Variation of the concentration of dimethyl mercury had no effect on the rate of reaction. The rate of formation of methane and ethane remained constant at constant intensity when the concentration of dimethyl mercury was increased by a factor of four, as shown by the data in Table II.

TABLE II  
EFFECT OF  $\text{Hg}(\text{CH}_3)_2$  CONCENTRATION  
Temperature = 25° C.;  $\text{C}_6\text{H}_{14} = \text{ca. } 10^{-2}$  mole

Expt.	$\text{Hg}(\text{CH}_3)_2$ (mole)	$\text{CH}_4$ (ml. (N.T.P.)/hr.)	$\text{C}_2\text{H}_6$ (ml. (N.T.P.)/hr.)	Time (hr.)
1	$4 \times 10^{-5}$	$6.7 \times 10^{-3}$	$1.5 \times 10^{-3}$	12
2	$8 \times 10^{-5}$	$6.8 \times 10^{-3}$	$1.4 \times 10^{-3}$	12
3	$2 \times 10^{-4}$	$6.8 \times 10^{-3}$	$1.5 \times 10^{-3}$	12
4*	$2 \times 10^{-4}$	$6.9 \times 10^{-3}$	$1.4 \times 10^{-3}$	17
5	$2 \times 10^{-4}$	$6.6 \times 10^{-3}$	$1.6 \times 10^{-3}$	12

\* Experiment using liquid thermostat. Volume of light in cell approximately half that in other experiments.

The effect of a 50-fold variation in light intensity on the rate of production of methane and ethane is given in Table III. Relative intensities are not explicitly stated for most runs but may be inferred from the values of  $R_{\text{CH}_4}$ . At the lower light intensities the amount of ethane produced was quite small and its determination was therefore less accurate than in the other experiments. Values of the ratios  $R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}$  and  $R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}^{\frac{1}{2}}$  are given in the table and it is seen that the data point clearly to the conclusion that the former ratio is more nearly independent of light intensity than the latter. In a few runs, Nos. 5-12, the optical system and lamp were unchanged and the intensity was varied by interposing filters. While the results are rather scattered, they indicate that within the experimental error both  $R_{\text{CH}_4}$  and  $R_{\text{C}_2\text{H}_6}$  are directly proportional to  $I$ .

Table IV summarizes the effect of temperature on the reaction. Between 25° C. and -80° C. the rate of production of ethane remains approximately constant whilst the rate of production of methane varies by a factor of three.

TABLE III  
EFFECT OF INTENSITY  
Temperature = 25° C.; Hg(CH<sub>3</sub>)<sub>2</sub> = ca. 10<sup>-4</sup> mole; C<sub>6</sub>H<sub>14</sub> = ca. 10<sup>-2</sup> mole

Expt.	$R_{CH_4}$ (ml. (N.T.P.)/hr.)	$I$ , relative	$R_{C_2H_6}$ (ml. (N.T.P.)/hr.)	$R_{CH_4}/R_{C_2H_6}$	$R_{CH_4}/R_{C_2H_6}^{\frac{1}{2}}$	Time (hr.)
1	$2.50 \times 10^{-2}$	—	$5.59 \times 10^{-3}$	4.5	0.34	21
2*	$2.51 \times 10^{-2}$	—	$5.71 \times 10^{-3}$	4.4	0.33	5
3	$1.80 \times 10^{-2}$	—	$4.29 \times 10^{-3}$	4.2	0.28	12
4	$1.90 \times 10^{-2}$	—	$4.42 \times 10^{-3}$	4.3	0.28	12
5	$6.90 \times 10^{-3}$	100	$1.50 \times 10^{-3}$	4.6	0.18	12
6	$6.76 \times 10^{-3}$	100	$1.62 \times 10^{-3}$	4.2	0.17	18
7	$4.60 \times 10^{-3}$	58	$6.94 \times 10^{-4}$	6.6	0.17	24
8	$4.10 \times 10^{-3}$	58	$7.70 \times 10^{-4}$	5.3	0.15	22
9	$1.35 \times 10^{-3}$	25	$2.91 \times 10^{-4}$	4.6	0.080	48
10	$1.19 \times 10^{-3}$	25	$3.28 \times 10^{-4}$	3.6	0.066	41
11	$1.01 \times 10^{-3}$	10	$1.10 \times 10^{-4}$	9.1	0.096	93
12	$5.53 \times 10^{-4}$	10	$1.08 \times 10^{-4}$	5.1	0.053	96
13**	$3.13 \times 10^{-3}$	—	$7.13 \times 10^{-4}$	4.4	0.12	14
14**	$6.87 \times 10^{-3}$	—	$1.43 \times 10^{-3}$	4.8	0.18	17
15	$4.99 \times 10^{-3}$	—	$1.16 \times 10^{-3}$	4.3	0.15	11

\* Experiments 1 and 2 carried out by R. G. Partington.

\*\* Experiments 13 and 14 using a liquid thermostat.

TABLE IV  
EFFECT OF TEMPERATURE  
Hg(CH<sub>3</sub>)<sub>2</sub> = ca.  $2 \times 10^{-4}$  mole; C<sub>6</sub>H<sub>14</sub> = ca. 10<sup>-2</sup> mole

Expt.	Time (hr.)	Temp. (° C.)	$R_{CH_4}$ (ml. (N.T.P.)/hr.)	$R_{C_2H_6}$ (ml. (N.T.P.)/hr.)	$R_{CH_4}/R_{C_2H_6}^{\frac{1}{2}}$	$\phi$
1a	14	25	$3.13 \times 10^{-3}$	$7.13 \times 10^{-4}$	4.4	4.5
2a	14	-30	$2.54 \times 10^{-3}$	$6.95 \times 10^{-4}$	3.6	3.9
3a	12	-60	$1.78 \times 10^{-3}$	$7.50 \times 10^{-4}$	2.4	3.3
4a	20	-80	$1.05 \times 10^{-3}$	$7.50 \times 10^{-4}$	1.4	2.5
5b	22	22	$3.72 \times 10^{-3}$	$8.11 \times 10^{-4}$	4.6	—
6b	22	-60	$2.01 \times 10^{-3}$	$8.28 \times 10^{-4}$	2.4	—
7c	17	25	$6.87 \times 10^{-3}$	$1.43 \times 10^{-3}$	4.8	—
8c	20	-60	$2.78 \times 10^{-3}$	$1.34 \times 10^{-3}$	2.1	—
9d	12	25	$7.03 \times 10^{-3}$	$1.50 \times 10^{-3}$	4.7	—
10d	12	-43	$4.78 \times 10^{-3}$	$1.74 \times 10^{-3}$	2.8	—

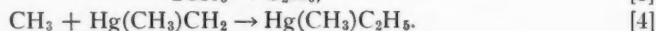
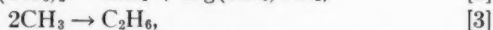
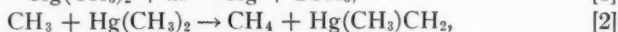
(a), (b), (c), (d) refer to sets of experiments with different lamps.

In experiments (d) the aluminum thermostat was used.

The relative over-all quantum yield of production of hydrocarbon ( $\phi$ ), i.e., CH<sub>4</sub> + 2C<sub>2</sub>H<sub>6</sub>, falls with temperature in one set of experiments from 4.5 at 25° C. to 2.5 at -80° C. All the experiments with the exception of experiments 9 and 10 were carried out using the liquid thermostat; in experiments 9 and 10 the aluminum thermostat was used.

#### DISCUSSION

The main steps in the mechanism of the gas-phase photolysis of mercury dimethyl are (2, 11)



In the presence of hexane, the reaction

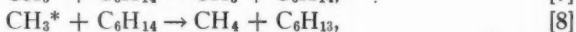
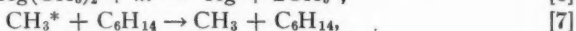
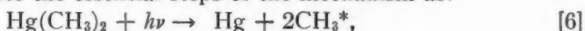


would also be expected (16). There are also certain complications in the mechanism whereby some additional ethane may be formed by a reaction of methyl radicals with mercury dimethyl (2). In the present case, however,  $R_{\text{C}_2\text{H}_6}$  is independent of the concentration of mercury dimethyl and such reactions cannot be important. Also, since the concentration of hexane is so much greater than that of mercury dimethyl, reaction [2] may be ignored relative to [5] as a source of methane. The mechanism in solution can therefore be considered to consist of reactions [1], [3], [5] and reactions whereby  $\text{C}_6\text{H}_{13}$  disappears by dimerization, disproportionation, or by reaction with methyl. Under these conditions

$$\frac{R_{\text{CH}_4}}{R_{\text{C}_2\text{H}_6}^{\frac{1}{2}}} = \frac{k_5}{k_3^{\frac{1}{2}}} [\text{C}_6\text{H}_{14}] = \text{const.} \frac{k_5}{k_3^{\frac{1}{2}}}$$

This relation is not obeyed, since  $R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}^{\frac{1}{2}}$  is not constant. Also if this were fulfilled the temperature coefficient of the ratio would be equal to  $E_5 - \frac{1}{2}E_3 \approx E_5 \approx 8$  kcal. Actually the temperature coefficient of methane production is very small, and corresponds to about 1 kcal. Also, in view of the magnitudes of  $E_5$  and  $E_2$  methane production would be expected to be negligible at low temperatures, instead of which it exceeds that of ethane at all temperatures.

It seems almost certain that these results are to be explained on the basis of "hot radicals." In reaction [1] excess energy of about 60 kcal. is available. We may therefore write the essential steps of the mechanism as:



together with steps involving the disappearance of  $\text{C}_6\text{H}_{13}$ . On this basis

$$\frac{R_{\text{CH}_4}}{R_{\text{C}_2\text{H}_6}} = \text{constant},$$

independent of  $[\text{Hg}(\text{CH}_3)_2]$ , and of intensity. Table III shows that this relationship is fulfilled. On such a basis also, an apparent activation energy of *ca.* 1 kcal. appears reasonable. (The positive temperature coefficient might, however, also be due to the diminished stability of  $\text{HgCH}_3$  at higher temperatures.)

It may therefore be concluded that hot radical reactions become predominant at very low temperatures in the present system, in spite of their relative unimportance in the gas-phase at higher temperatures.

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# ATISINE: THE HETEROCYCLIC RING AND FUNCTIONAL GROUPS<sup>1</sup>

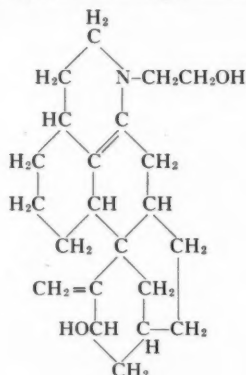
BY O. E. EDWARDS AND TARA SINGH<sup>2</sup>

## ABSTRACT

Evidence is presented which confirms the presence in atisine and isoatisine of vinylamine double bonds, an N-( $\beta$ -hydroxyethyl) group, an exocyclic methylene group, and a secondary hydroxyl in an allylic relation to the latter. The size and substitution of the heterocyclic ring is discussed. The pyrolysis of atisine and isoatisine hydrochlorides to give a  $C_{20}H_{29}ON$  base is described.

## INTRODUCTION

The alkaloid atisine is of interest as a representative of the less oxygenated aconite group (kobusine, talatisine, napelline, and hetisine are others). It is a dihydroxy pentacyclic base of empirical formula  $C_{22}H_{33}O_2N$  containing two double bonds (10). The nitrogen is tertiary, and is substituted by a group which can give ethyl iodide in the Herzig-Meyer N-alkyl determination (7). On the basis of information obtained by oxidative degradation and selenium dehydrogenation Jacobs put forward a tentative structure (Formula 1) for the base (9). In work preliminary to systematic degradation of the alkaloid we have



FORMULA 1

provided proof of the presence of some of the structural features postulated by Jacobs.<sup>3</sup>

Jacobs and co-workers demonstrated that atisine was a very strong base (7), that it was isomerized by alkali to a weaker base, isoatisine (7, 11), and that both bases could be converted by prolonged heating with sodium hydroxide in methanol to dihydroatisine (11). They interpreted the isomerization as migration of a vinylamine double bond from one side of the nitrogen to the

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<sup>2</sup> National Research Council Postdoctorate Fellow.

<sup>3</sup> A preliminary report of some of this work was published earlier (6).



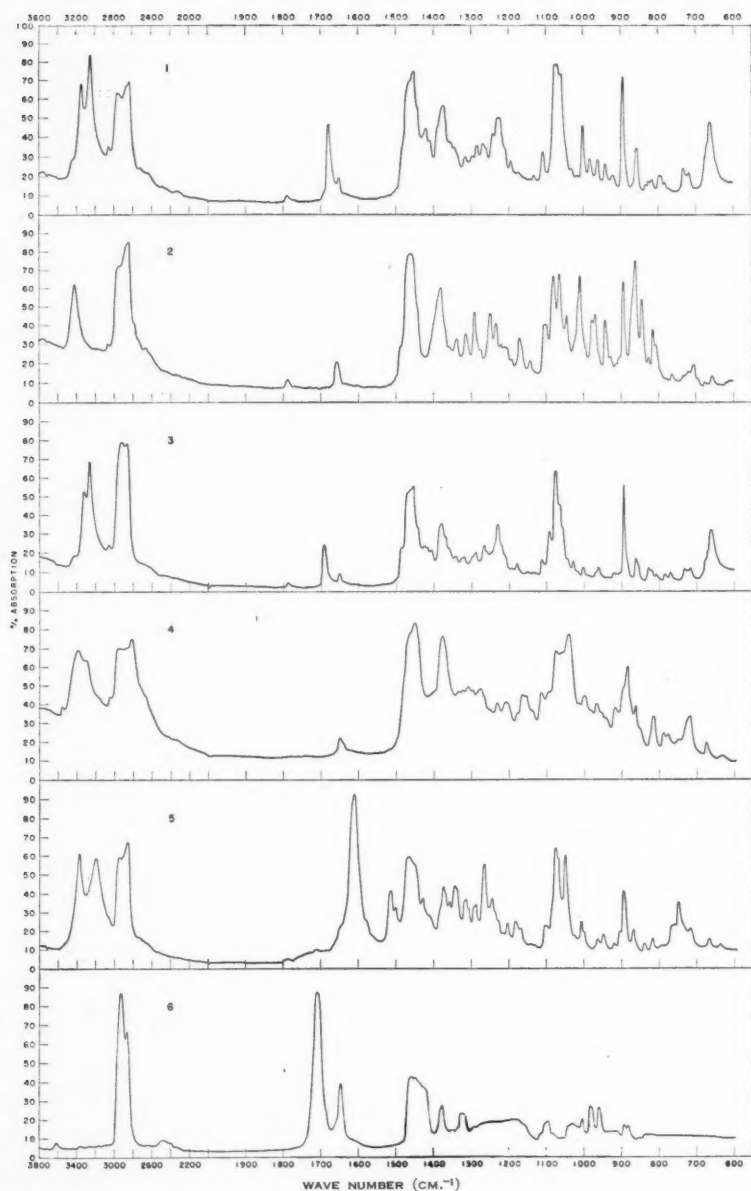


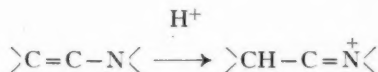
FIG. 1. Infrared spectra.

1. Atisine hydrochloride (nujol mull). 2. Isoatisine (nujol mull). 3. Isoatisine hydrochloride (nujol mull). 4. Dihydroatisine (nujol mull). 5. Oxoatisine (nujol mull). 6. The  $C_{20}H_{29}ON$  base in chloroform (6.4 mgm. per ml., 1 mm. cell).

NOTE ADDED IN PROOF: The wave numbers at the top of the figure, between 2000 and 3600  $cm^{-1}$  are displayed one division to the left.

other, and the formation of the dihydroatisine as reduction of the vinylamine double bond.<sup>4</sup>

Adams and Mahan showed that simple tertiary vinylamines are stronger by several pK units than the corresponding saturated amines. They suggested that this was due to the formation of salts with quaternary ammonium character (1).



We have demonstrated that atisine (pK 12.2)<sup>5</sup> and isoatisine (pK 10.0) are stronger bases than dihydroatisine (pK 8.2) as would be expected if Jacobs' postulate were correct. The infrared spectra (mulls) of atisine and isoatisine hydrochlorides contain bands at 1680 cm.<sup>-1</sup> and 1692 cm.<sup>-1</sup> respectively, which are absent in the parent bases (Fig. 1). Such bands are characteristic of salts containing the  $\text{>C=N}^+\text{<}$  group (4, 13).

Saturated tertiary bases show more intense absorption in the ultraviolet above 220 mμ than the corresponding hydrochlorides or perchlorates (4, 5). The converse seems to be true for aliphatic bases whose salts contain the  $\text{>C=N}^+\text{<}$  chromophore (4). Both atisine and isoatisine fall into the latter category (Fig. 2).

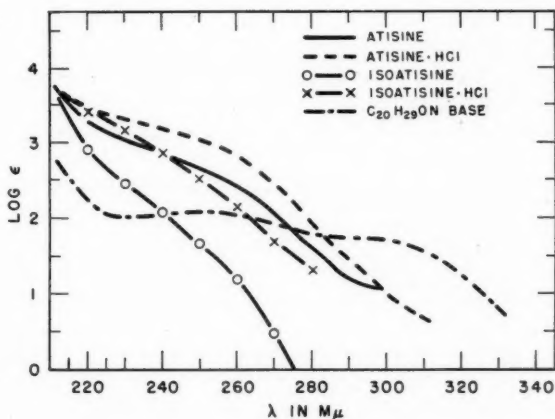


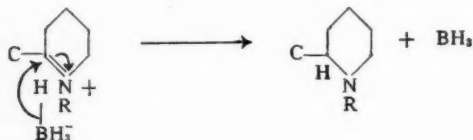
FIG. 2.

Finally, evidence for the vinylamine character of the isomeric bases comes from the fact that both could readily be reduced by sodium borohydride to the same dihydroatisine obtained on drastic alkali treatment of the bases (11). This can be considered as reduction of a small percentage of the carbinol-

<sup>4</sup>This is not a simple analogue of the Cannizzaro reaction, since the yield of reduced product is 75%. Hence oxidation of methanol probably accompanies the reduction of the alkaloid.

<sup>5</sup>The pK values were determined in 50% aqueous methanol solution.

amine form present in aqueous methanol solution, or as reduction of the salt form (always present in polar solvents) as shown:



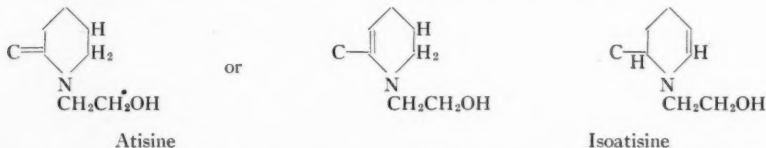
Huebner and Jacobs (7) showed that a two carbon fragment and one oxygen were rather readily eliminated from atisine by heating with nickel on alumina. They also found that the lactam tricarboxylic acid from isoatisine lost a  $C_2H_2O_2$  fragment when treated with thionyl chloride (8, 9). Jacobs concluded that a  $>NCH_2CH_2OH$  group was present in atisine. It seems reasonable that such a group could give ethyl iodide in the Herzig-Meyer determination (7).

Wiesner and co-workers (3) heated atisine at  $300^\circ$  with selenium and obtained the same  $C_{20}H_{29}ON$  base obtained by Huebner and Jacobs with nickel on alumina. They found it to contain an imino and a carbonyl group. When this base was reduced to the secondary amine and the product condensed with ethylene chlorohydrin a base isomeric with tetrahydroatisine was obtained. Thus supporting evidence, but not decisive proof of the presence of the ethanolamine structure had been presented.

Leonard and Rebenstorf have shown (12) that simple  $\beta$ -(dialkylamino)-ethanols are cleaved by lead tetraacetate at  $60^\circ$  to a glycolic aldehyde derivative. This reaction has now been applied to tetrahydroatisine, and glyoxal bis-*p*-nitrophenylhydrazone obtained in 31% yield from the products. This provides decisive confirmation of the presence of the ethanolamine system in the alkaloid.

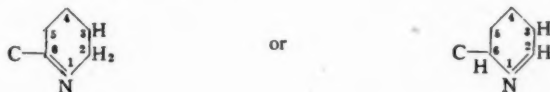
Since isoatisine could be oxidized to a lactam with disappearance of the vinylamine double bond, while atisine gave a lactam retaining its vinylamine bond, Jacobs concluded (9) that in atisine there are two hydrogens on one ring carbon  $\alpha$  to the nitrogen but none on the other. An examination of the infrared spectrum of oxoisoatisine has shown the lactam carbonyl band to be at  $1610\text{ cm}^{-1}$ . This suggests that the heterocyclic ring is six membered<sup>6</sup> with hydrogen bonding to the carbonyl lowering the frequency from the usual position near  $1640\text{ cm}^{-1}$ . An active hydrogen determination on isoatisine confirmed that there are two hydroxyls in this base, as in atisine.

Thus the heterocyclic ring in the bases can be written as:



<sup>6</sup> Unpublished results in this laboratory indicate that saturated five membered lactams absorb near  $1690\text{ cm}^{-1}$ .

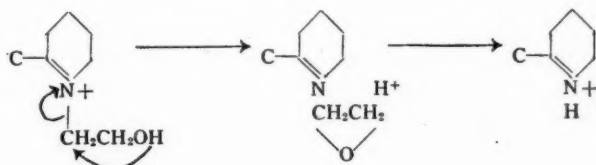
The fact (3) that atisine when heated with selenium at 300° gives considerable material containing the system



must mean that the heterocyclic ring cannot aromatize without carbon migration. There cannot be meta bridging from carbons 4 to 6, or 3 to 5 in this ring since then either atisine or isoatsine would have a bridgehead double bond (Bredt's rule violated). Thus the most likely explanation of the failure to aromatize is that carbon 4 or 5 is quaternary. The formula for atisine postulated by Jacobs does not contain this feature, hence doubt is cast on its validity.

The infrared spectra of atisine, isoatsine, and dihydroatsine contain bands characteristic of an exocyclic methylene group (2) at 894  $\text{cm}^{-1}$ , 1650  $\text{cm}^{-1}$ , and 3060  $\text{cm}^{-1}$ , thus confirming Jacobs' interpretation of his oxidation studies.

It seemed probable that the pyrolysis of atisine or isoatsine salts would proceed smoothly with elimination of the N-( $\beta$ -hydroxyethyl) side chain:



Actually, when either salt was heated at 310° a mixture was obtained. When the base liberated from this was chromatographed on alumina, the fraction rapidly eluted by benzene crystallized readily. When recrystallized from petroleum ether it melted at 82–84° and analyzed correctly for  $\text{C}_{20}\text{H}_{29}\text{ON}$ . On repeated recrystallization from the same solvent a small amount of material melting at 142° was obtained. The 84° base gave a picrate melting at 252°, from which base melting at 84° could be recovered. The infrared spectra of the 84° and 142° samples were nearly identical, containing a carbonyl band at 1707  $\text{cm}^{-1}$  and what is probably an imino band at 1646  $\text{cm}^{-1}$  (Fig. 1). Thus in the light of the above evidence, and of the fact that the 84° base has an ultraviolet spectrum (Fig. 2) very similar to that published by Huebner and Jacobs for the  $\text{C}_{20}\text{H}_{29}\text{ON}$  compound, it is most likely that it is a stereoisomer of the base described by the previous workers (3, 7).

The  $\text{C}_{20}\text{H}_{29}\text{ON}$  base could be reduced in acid solution in the presence of platinum to a dihydro derivative. This was still a ketone (band at 1710  $\text{cm}^{-1}$ ) but the band at 1646  $\text{cm}^{-1}$  in the infrared and the ultraviolet maximum at 250  $\text{m}\mu$  (Fig. 2) were no longer present. This is consistent with reduction of a  $>\text{C}=\text{N}-$  group in the base.

The bands which can be assigned to an exocyclic methylene group in atisine and isoatisine are absent in the  $C_{20}H_{29}ON$  base and a clear band due to a methyl group ( $1376\text{ cm}^{-1}$ ) is present in the infrared spectrum of chloroform solutions of the  $C_{26}H_{29}ON$  and the dihydro bases. Thus it appears that Jacobs' suggested relation of the exocyclic methylene to the secondary hydroxyl is correct, and that the allylic system is readily isomerized by heat and probably by acid (7) to the corresponding ketone. The position of the carbonyl band in the infrared makes it probable that it is on a six membered or larger ring.

The reactions in the heterocyclic ring are very stereospecific. Only one isomer is formed when the vinylamine double bond in atisine is reduced chemically and when it is isomerized to give isoatisine. Thus the mixture of stereoisomers formed on catalytic reduction of atisine, isoatisine, and dihydroatisine is most probably due to the two orientations of the new methyl group.

Systematic degradation of the alkaloid, using the various functional groups, is projected.

#### EXPERIMENTAL

Ultraviolet spectra were determined on a Beckman DU spectrophotometer. Infrared spectra were obtained using a Perkin-Elmer model 21 double beam spectrophotometer. The pK's were determined by titration of the bases with 0.05 *N* hydrochloric acid in 50% aqueous methanol, using the same mixture as solvent.

##### Atisine

The alkaloid was isolated from the roots of *Aconitum heterophyllum* obtained from the S. B. Penick Co. The finely ground root was percolated at room temperature with methanol. Removal of the solvent from the extract was carried out under reduced pressure. Crystalline sugar which separated from a concentrated methanol solution of the residue was removed by filtration, the filtrate reduced to a sirup, and the alkaloids separated by the method of Jacobs and Craig (10). Fifty pounds of root yielded approximately 63 gm. of atisine hydrochloride.

The recrystallized hydrochloride had the form of needles, m.p.  $303^{\circ}$  dec. (immersed at  $190^{\circ}$ ),  $[\alpha]_D^{25} 28 \pm 1^{\circ}$  ( $c = 1.6$  in water). The infrared spectrum (Fig. 1) contained bands at 3060, 1652, and  $895\text{ cm}^{-1}$  ( $>C=CH_2$ ) and at  $1680\text{ cm}^{-1}$  ( $>C=\overset{+}{N}<$ ).

The base liberated from the salt with aqueous sodium hydroxide and extracted into ether was a colorless glass. Its infrared spectrum (film) had bands at 3060, 1652, and  $895\text{ cm}^{-1}$  ( $>C=CH_2$ ). It had a pK of  $12.2 \pm 0.2$ . A sample of the base distilled at  $110^{\circ}$  under  $5 \times 10^{-4}$  mm. had  $[\alpha]_D -21 \pm 2^{\circ}$  ( $c = 2.4$  in carbonate-free ethanol). Its infrared spectrum (film) contained bands at 1020 and at  $865\text{ cm}^{-1}$  not present in the base as described above, hence changes appear to have taken place on distillation. Found: active hydrogen, 0.567, 0.541. Calc. for  $C_{22}H_{33}O_2N$ : two active hydrogens, 0.587.

##### Isoatisine

This was prepared by the methods of Jacobs and Craig (11) and recrystallized from aqueous methanol. It melted at  $152^{\circ}$  after softening at  $148^{\circ}$ , and had

a pK of 10.0. Its infrared spectrum had bands at 3070, 1656, and 894  $\text{cm}^{-1}$  ( $>\text{C}=\text{CH}_2$ ) (Fig. 1). Found: active hydrogen, 0.530, 0.592. Calc. for  $\text{C}_{22}\text{H}_{33}\text{O}_2\text{N}$ : two active hydrogens 0.587. The hydrochloride had the form of needles, m.p. 296° dec. (immersed at 260°),  $[\alpha]_D -1 \pm 1^\circ$  ( $c = 1.0$  in ethanol). It showed no mixed melting point depression with atisine hydrochloride. Its infrared spectrum (mull) had bands at 3060, 1650, and 894  $\text{cm}^{-1}$  ( $>\text{C}=\text{CH}_2$ ) and at 1692  $\text{cm}^{-1}$  ( $>\text{C}=\text{N}^+<$ ).

#### *Dihydroatisine*

(a) To a solution of 50 mgm. of atisine hydrochloride in 5 cc. of 80% methanol-water was added 30 mgm. of sodium borohydride. There was brisk evolution of hydrogen. The solution stood at room temperature for 1.5 hr. after which the solvent was removed under reduced pressure. The residue was extracted with ether. The dried concentrated ether solution deposited rhombic plates (45 mgm.) m.p. 157–159°. This did not depress the melting point of the products from (b) and (c).

(b) Isoatisine (108 mgm.) in 10 cc. of 80% methanol-water containing 63 mgm. of sodium borohydride was left at room temperature for 1.5 hr. The product was isolated as in (a). Yield, 100 mgm. in three crops. The first crop of crystals melted at 157–159°,  $[\alpha]_D -45.4 \pm 0.5^\circ$  ( $c = 2.72$  in ethanol), pK, 8.2. Found: C, 76.32; H, 9.95. Calc. for  $\text{C}_{22}\text{H}_{36}\text{O}_2\text{N}$ : C, 76.47; H, 10.22. Infrared bands (mull) at 3050, 1650, and 886  $\text{cm}^{-1}$  ( $>\text{C}=\text{CH}_2$ ) (Fig. 1).

(c) Atisine hydrochloride (100 mgm.) was added to 5 cc. of a hot saturated solution of sodium hydroxide in methanol in a pressure tube. The tube was sealed and heated at 100° for 90 hr. with occasional shaking. The mixture was then diluted with 15 cc. of water and the base extracted with ether. From the dried concentrated ether solution 40 mgm. of rhombic plates were obtained, m.p. 152–154° with previous sintering. This gave no mixed melting point depression with the products from (a) and (b).

The three samples had identical infrared spectra.

#### *Dihydroatisine Hydrochloride*

This crystallized from methanol as prisms, m.p. 261–263°. Its infrared spectrum (mull) had no  $>\text{C}=\text{N}^+<$  band between 1660 and 1700  $\text{cm}^{-1}$ .

#### *Tetrahydroatisine*

Two hundred and fifty milligrams of atisine hydrochloride in 50 cc. of methanol in the presence of platinum from 50 mgm. of platinum oxide (Adams) absorbed 31.6 cc. of hydrogen in seven minutes (27.5°C., 1 atm.). The catalyst was removed by filtration and the solvent evaporated. The residue was taken up in sodium hydroxide solution and extracted with ether. The dried and concentrated ether solution deposited 150 mgm. of small needles, m.p. 155–160°. When recrystallized from ethanol this gave 40 mgm., m.p. 170–172° after preliminary softening. Jacobs and Craig record a melting point of 173° (11). Its infrared spectrum (mull) contained no band in the 1600–1700  $\text{cm}^{-1}$  region and no band near the 890  $\text{cm}^{-1}$ .

*Glyoxal from Tetrahydroatisine*

A solution of 250 mgm. of tetrahydroatisine (m.p. 150°) and 650 mgm. (2 molar equivalent) of lead tetraacetate in 25 cc. of glacial acetic acid was heated at  $62 \pm 4^\circ$  for 24 hr. All the lead tetraacetate was consumed. The mixture was diluted with 25 ml. of water and 500 mgm. of *p*-nitrophenylhydrazine added. The resulting solution was filtered and then heated on the steam bath for four hours. The red crystalline precipitate (25 mgm.) melted at 310° dec. This was sparingly soluble in glacial acetic acid but was recrystallized from the boiling solvent, m.p. 311–312° dec. Found: C, 51.25; H, 3.65. Calc. for  $C_{14}H_{12}N_6O_4$ : C, 51.21; H, 3.66. This compound did not depress the melting point of authentic glyoxal bis(*p*-nitrophenyl)-hydrazone, and the two specimens had identical infrared spectra.

On further heating (15 hr.) the filtrate from the first crop of osazone gave 50 mgm. more of the osazone (total, 31% of theory).

*Pyrolysis of Atisine Hydrochloride*

Atisine hydrochloride (400 mgm.) was immersed in a metal bath at 310–320°C. and held at that temperature for 1.5 min. The dark brown product was extracted with dilute hydrochloric acid and filtered after the addition of charcoal. The filtrate was made alkaline with sodium hydroxide and extracted with benzene. The benzene solution on evaporation yielded 230 mgm. of base, which was again dissolved in benzene, then adsorbed on 3 gm. of alkaline alumina (activity 1). The first 20 cc. of benzene eluted 133 mgm., and the following four 20 cc. portions eluted 40 mgm. more. This material slowly solidified. When crystallized from petroleum ether the compound melted at 82–84° with previous shrinking. Found: C, 80.61; H, 9.77. Calc. for  $C_{20}H_{29}ON$ : C, 80.22; H, 9.76. Ultraviolet spectrum (Fig. 2):  $\lambda_{\max}$  250 m $\mu$ ,  $\log \epsilon$  2.09; shoulder at 295 m $\mu$ ,  $\log \epsilon$  1.74. Its infrared spectrum (chloroform) had bands at 1646 and 1707  $\text{cm}^{-1}$  (Fig. 1).

*Pyrolysis of Isoatisine Hydrochloride*

When 380 mgm. of isoatisine hydrochloride was treated as above, 190 mgm. of base was recovered. This gave 139 mgm. of the readily eluted base. After one recrystallization from petroleum ether this melted at 83–85°. It proved identical with the product from atisine hydrochloride (mixed melting point and comparison of infrared spectra).

The samples melting at 84° or 85° from both salts on repeated recrystallization from petroleum ether gave small quantities of base melting at 142° after previous sintering. The infrared spectrum of this material showed only minor differences in the fingerprint region from that of the 85° base.

The combined 85° base prepared from both salts was converted to the picrate. This crystallized from ethanol as long needles, m.p. 250–252°. Found: C, 59.20; H, 6.16. Calc. for  $C_{26}H_{32}O_8N_4$ : C, 59.08; H, 6.10. Base recovered from the pure picrate and crystallized from petroleum ether melted at 80–84°.

*Dihydro-keto Base*

$C_{20}H_{29}ON$  base (25 mgm.) in 3 cc. of ethanol containing three drops of concentrated hydrochloric acid in the presence of platinum from 10 mgm. of



platinum oxide (Adams) absorbed 2.08 cc. of hydrogen in eight hours at 26°C. and 761.5 mm. pressure (mole ratio 1.0). The product crystallized as prisms from petroleum ether, m.p. 135°. Found: C, 79.22; H, 9.99. Calc. for  $C_{20}H_{31}ON$ : C, 79.67; H, 10.37. Ultraviolet spectrum:  $\lambda_{min}$  266  $m\mu$ ,  $\log \epsilon$  1.74;  $\lambda_{max}$  291  $m\mu$ ;  $\log \epsilon$  1.91. Infrared spectrum (chloroform) had bands at 1710  $cm^{-1}$  and at 1376  $cm^{-1}$ .

#### ACKNOWLEDGMENT

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# ADDITION OF METHYL RADICALS TO UNSATURATED HYDROCARBONS<sup>1</sup>

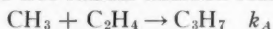
BY L. MANDELCORN<sup>2</sup> AND E. W. R. STEACIE

## ABSTRACT

The rates of addition of methyl radicals, produced by the photolysis of acetone between 140° C. and 240° C., to unsaturated hydrocarbons were determined by two independent methods. From the kinetics of the addition and the methyl radical combination reactions, addition of methyl radicals to ethylene, propylene, acetylene, and butadiene was found to proceed with activation energies of 7.0, 6.0, 5.5, and ~2.5 kcal. respectively and steric factors of the order of 10<sup>-4</sup>.

## INTRODUCTION

The kinetics of a simple free radical addition reaction such as

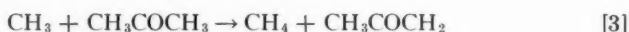


are generally difficult to investigate because of complications arising from the various other reactions in which the reactants also participate, and from the nature of the product, which is a free radical. The main difficulty obviously lies in the tendency for the unsaturated hydrocarbon to polymerize, which may obscure the fate of the free radicals in the system, and often prevents quantitative study of any single process.

In this investigation the unsaturated hydrocarbons were kept at as low concentrations as possible to prevent them from participating in reactions other than addition by methyl radicals.

### *Methods of Determining the Rate of Addition*

In a previous paper (5) it was shown that almost all the methyl radicals in the photolysis of acetone between 100° C. and 284° C. are accounted for by the following reactions:



This conclusion was based on the fact that, within 3%,

$$(2R_{\text{C}_2\text{H}_6} + R_{\text{CH}_4} + R_{\text{CH}_3\text{COC}_2\text{H}_5})/R_{\text{CO}} = 1.90,$$

where  $R_X$  is the rate of formation of the product X. It follows that, if in the presence of an unsaturated hydrocarbon the only other reaction of methyl radicals is addition, and  $R_{\text{CO}}$  is unaffected, the rate of addition, designated as  $R'_A$  for this method, may be obtained from

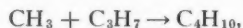
$$(2R_{\text{C}_2\text{H}_6} + R_{\text{CH}_4} + R_{\text{CH}_3\text{COC}_2\text{H}_5} + R'_A)/R_{\text{CO}}$$

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<sup>2</sup> National Research Council of Canada Postdoctorate Fellow 1951-53.

equated to the ratio obtained in the absence of unsaturated hydrocarbon. However, methyl radicals may combine with the product of addition, i.e.



thereby making  $R'_A$  higher than the true rate of addition. But unless the methyl radical concentration is controlled only by the addition reaction, which is not so here, this reaction will decrease and diminish in effect on  $R'_A$  with increasing temperature, and will lead to too low a value for  $E_A$ .

Since ethane and methane account for most of the methyl radicals produced, it would be expected that the greatest effect on the material balance of the addition reaction is on the  $2R_{\text{C}_2\text{H}_6} + R_{\text{CH}_4}$  portion. Therefore it would appear possible to evaluate the rate of addition from

$$(2R_{\text{C}_2\text{H}_6} + R_{\text{CH}_4} + R''_A)/R_{\text{CO}}$$

equated to  $(2R_{\text{C}_2\text{H}_6} + R_{\text{CH}_4})/R_{\text{CO}}$  in the absence of unsaturated hydrocarbon. By comparing  $R''_A$  with  $R'_A$  it can be seen that the former will be lower, the difference between the two depending on the magnitude of  $R_{\text{CH}_3\text{COC}_2\text{H}_5}/R_{\text{CO}}$  and the extent to which it is decreased by the addition reaction.  $R''_A$  may therefore be lower than  $R'_A$ , especially when the amount of addition is large, i.e., at high temperatures.

The other method used is based on the assumption that the rate of addition of methyl radicals is equal to the rate of disappearance of unsaturated hydrocarbon. Because of polymerization and, possibly, addition by acetyl radicals,  $R'''_A$ , the rate obtained by this method, should be higher than the true rate of addition of methyl radicals, these effects being accentuated with increasing temperature. Although the unsaturated hydrocarbon may also disappear by methyl radical abstraction of hydrogen atoms, the rate of abstraction can be calculated from the ratio  $R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}^{1/2}$  in the presence and absence of the olefin. It is obvious that if hydrogen abstraction occurs to any large extent the rates of addition obtained by the material balance method lose much of their significance.

The limitations of the two methods are such that activation energies based on  $R'_A$  and  $R''_A$  will be low while those obtained from  $R'''_A$  will be high. Since these methods are also essentially independent, the extent to which the results agree will be an indication of their validity.

#### EXPERIMENTAL

The apparatus was essentially the same as that reported previously (5). Most experiments were done with the reaction cell separated from the rest of the apparatus by a stopcock situated very close to the furnace, the volumes of the cell and connecting tubing being 195 cc. and 10 cc. respectively. Some experiments, as indicated in the tables, were done with the cell isolated by a mercury cutoff, the volume of the connecting tubing being 37 cc.

The following unsaturated hydrocarbons were used: ethylene, propylene, butadiene (Philips Research Grade), and acetylene (Ohio Chemical and Mfg. Co.). Ethylene, propylene, and acetylene were degassed by bulb to bulb distil-

lation at  $-196^{\circ}\text{C}$ . and the second of three fractions coming over at  $-80^{\circ}\text{C}$ . was retained. Butadiene was degassed at  $-196^{\circ}\text{C}$ . and  $-116^{\circ}\text{C}$ . and fractionated at  $-30^{\circ}\text{C}$ . Some experiments were done with deuterated acetylene ( $\text{C}_2\text{D}_2$ ), primarily to see if there was hydrogen abstraction from acetylene. The deuterated acetylene was prepared by the action of  $\text{D}_2\text{O}$  on calcium carbide.

Because acetylene absorbs wave lengths below  $2200\text{ \AA}$ , the light from the Hanovia S-100 lamp was filtered with a Corning No. 7910 filter for that series of experiments. Since it was found that this filter had no significant effect on the material balances, the data for acetone alone, which were obtained with this filter, were used as reference in determining  $R''_A$  for ethylene and propylene where no filter was used. In the series of experiments with butadiene a Corning No. 9863 filter was used throughout to avoid any photopolymerization of butadiene, which absorbs light at  $2300\text{ \AA}$  and below. It should be noted that the light intensities, or  $R_{\text{CO}}$ , in the reference experiments and in those with unsaturated hydrocarbon were within 10% of each other. The precaution of keeping the light intensity constant for both experiments was taken since it was found that the material balance  $(2R_{\text{C}_2\text{H}_6} + R_{\text{C}_2\text{H}_4})/R_{\text{CO}}$  varies slightly with light intensity (5). Irradiation time was invariably one hour.

The analytical procedure was also similar to that reported previously (5) except that it was extended to determine a larger range of components, notably the amount of unsaturated hydrocarbon remaining at the end of an experiment. It was noted that by removing the products condensable at  $-116^{\circ}\text{C}$ . in a trap situated before the analytical system, separation of the components that are volatile at lower temperatures was more rapid.

In the experiments with ethylene, methane and carbon monoxide were separated at the temperature of solid nitrogen since ethylene distills slowly at  $-196^{\circ}\text{C}$ ., the temperature of liquid nitrogen. The  $\text{C}_2$ ,  $\text{C}_3$ , and  $\text{C}_4$  fractions were separated at  $-180^{\circ}\text{C}$ .,  $-160^{\circ}\text{C}$ ., and  $-130^{\circ}\text{C}$ . respectively and analyzed with a mass spectrometer. It was found in the experiments with propylene that ethane and propylene could be separated effectively at  $-180^{\circ}\text{C}$ . and  $-160^{\circ}\text{C}$ . With acetylene present, fractions were removed at  $-180^{\circ}\text{C}$ .,  $-150^{\circ}\text{C}$ ., and occasionally at  $-130^{\circ}\text{C}$ . and analyzed for  $\text{C}_2$ , carbon monoxide,  $\text{C}_3$ , and  $\text{C}_4$  with the mass spectrometer. Acetylene appeared to retain some of the carbon monoxide at the temperature of liquid nitrogen. This observation was confirmed by photolyzing two separate samples of acetone, adding some acetylene at the end of the photolysis of one to the acetone and its products while they were still in the reaction cell, and analyzing both as in a typical experiment with acetylene. No analyses were made for butadiene remaining at the end of an experiment.

## RESULTS

The rate constants appearing in the tables were calculated on the basis of the addition reaction and reaction [2], e.g.

$$\frac{k''_A}{k_2^{1/2}} = \frac{R''_A}{R_{\text{C}_2\text{H}_6}^{1/2}[\text{C}_2\text{H}_4]},$$

and are expressed as  $\text{cm}^{3/2} \text{ molecule}^{-1/2} \text{ sec}^{-1/2}$ . The concentration of unsaturate

is the average during the photolysis. Arrhenius plots gave  $E_A - \frac{1}{2}E_2$  and from these the  $P_A/P_2^{\frac{1}{2}}$  ratios, or relative steric factors, were obtained. Since it has been shown that for methyl radical combination, i.e. reaction [2],  $E_2 \sim 0$  and  $P_2 \sim 1$  (4), the activation energies and steric factors correspond to the addition reaction.

In Table I are shown the material balances for the photolysis of acetone alone.

TABLE I  
MATERIAL BALANCES IN THE PHOTOLYSIS OF ACETONE

Temp., ° C.	$R_{C_2H_6}$	$R_{CH_4}$	$R_{CH_3COC_2H_5}$	$R_{CO}$	$2R_{C_2H_6} + R_{CH_4}$	$2R_{C_2H_6} + R_{CH_4} + R_{CH_3COC_2H_5}$
	$\times 10^5$ cc. N.T.P./sec.				$R_{CO}$	$R_{CO}$
(a)						
<i>Acetone conc. = <math>1.76 \times 10^{-6}</math> M./cc.</i>						
144	6.55	1.81	—	8.39	1.78	
177	4.99	3.73	—	8.59	1.60	
189	5.51	5.34	—	10.19	1.61	
204	4.25	6.55	—	10.05	1.50	
205	4.89	7.03	—	11.02	1.53	
241	2.69	11.18	—	11.57	1.43	
286	1.56	16.66	—	13.62	1.45	
<i>Acetone conc. = <math>0.9 \times 10^{-6}</math> M./cc.</i>						
159	3.21	.98	—	4.36	1.70	
175	3.36	1.54	—	4.94	1.67	
199	2.78	2.51	—	5.09	1.58	
219	2.18	3.29	—	5.21	1.47	
(b) (No. 9863 filter)						
<i>Acetone conc. = <math>1.76 \times 10^{-6}</math> M./cc.</i>						
164.5	7.08	2.98	—	10.24	1.67	
180	7.10	4.39	—	11.49	1.62	
200	4.63	6.40	—	10.41	1.50	
236	2.55	10.36	—	10.37	1.49	
(c) (No. 9863 filter)						
<i>Acetone conc. = <math>1.76 \times 10^{-6}</math> M./cc.</i>						
144	6.06	1.70	1.2	7.72	1.79	1.95
183	3.29	2.90	1.9	5.98	1.59	1.89
240	1.34	6.41	2.3	6.11	1.48	1.86

Since the rates of addition are based on differences between relatively large quantities, small analytical errors could cause large deviations in the calculated rates of addition. The analytical accuracy was, however, better than  $\pm 0.10 \times 10^{-5}$  cc. N.T.P. per sec. and reproducibility of  $k''_A/k_2^{\frac{1}{2}}$  and  $k'''_A/k_2^{\frac{1}{2}}$  was accordingly  $\pm 20\%$  at the lower temperatures and  $\pm 5\%$  at the higher temperatures. These deviations correspond to  $\pm 1$  kcal. in the activation energies, which is consistent with the accuracy of the Arrhenius plots.

In each series of experiments at least one reference photolysis of acetone was done in the same period of time as the corresponding photolysis of acetone with

TABLE II  
PHOTOLYSIS OF ACETONE AND ETHYLENE (REF. TABLE I, c)

Temp., °C.	[C <sub>2</sub> H <sub>4</sub> ] init.		[C <sub>2</sub> H <sub>4</sub> ] fin.		R <sub>C<sub>2</sub>H<sub>6</sub></sub>		R <sub>C<sub>2</sub>H<sub>4</sub></sub>		R <sub>CH<sub>3</sub>COCH<sub>3</sub>H<sub>6</sub></sub>		R <sub>CO</sub>		R <sub>C<sub>2</sub></sub>		R' <sub>A</sub>		R'' <sub>A</sub>		R''' <sub>A</sub>		$\frac{k'_A}{k_2^{\frac{1}{2}}}$		$\frac{k''_A}{k_2^{\frac{1}{2}}}$		$\frac{k'''_A}{k_2^{\frac{1}{2}}}$	
	$\times 10^6$ M./cc.		$\times 10^6$ M./cc.		$\times 10^6$ cc. N.T.P./sec.		$\times 10^{12}$ cm. <sup>3</sup> /2 molecule <sup>-1</sup> sec. <sup>-1</sup>		$\times 10^{12}$ cm. <sup>3</sup> /2 molecule <sup>-1</sup> sec. <sup>-1</sup>		$\times 10^{12}$ cm. <sup>3</sup> /2 molecule <sup>-1</sup> sec. <sup>-1</sup>		$\times 10^{12}$ cm. <sup>3</sup> /2 molecule <sup>-1</sup> sec. <sup>-1</sup>		$\times 10^{12}$ cm. <sup>3</sup> /2 molecule <sup>-1</sup> sec. <sup>-1</sup>		$\times 10^{12}$ cm. <sup>3</sup> /2 molecule <sup>-1</sup> sec. <sup>-1</sup>		$\times 10^{12}$ cm. <sup>3</sup> /2 molecule <sup>-1</sup> sec. <sup>-1</sup>		$\times 10^{12}$ cm. <sup>3</sup> /2 molecule <sup>-1</sup> sec. <sup>-1</sup>		$\times 10^{12}$ cm. <sup>3</sup> /2 molecule <sup>-1</sup> sec. <sup>-1</sup>		$\times 10^{12}$ cm. <sup>3</sup> /2 molecule <sup>-1</sup> sec. <sup>-1</sup>	
144*	0.072	0.068	0.072	0.068	4.76	1.58	1.2	6.68	0.0	0.8	0.9	0.8	10	11	10	11	10	11	10	11	10	11	10	11	10	11
184	0.082	0.066	0.082	0.066	2.89	2.81	1.5	6.23	0.2	1.7	1.3	2.0	25	20	25	20	30	20	30	20	30	20	30	20	30	20
240	0.082	0.056	0.082	0.056	1.02	5.70	1.9	6.48	1.1	2.4	1.8	3.4	53	41	53	41	74	41	74	41	74	41	74	41	74	41

\* Used mercury cutoff for cell.

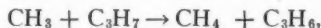
unsaturated hydrocarbon. No significant change in  $R_{CO}$  was observed with the addition of unsaturated hydrocarbon, thereby indicating the absence of addition of acetyl radicals. This was probably due to the low concentrations of unsaturated hydrocarbon, since Volman and Graven (10) found that larger concentrations of butadiene decreased  $R_{CO}$  in the photolysis of acetone.

Because each of the hydrocarbons manifested certain particular characteristics, their results will be given separately.

### Ethylene

Because of its importance, ethylene was studied more thoroughly than the other hydrocarbons. Emphasis was placed on ascertaining the validity of the methods used in determining the rate of addition and on the analysis of products.

The  $C_3$  fraction (Table II) consisted of propane and propylene, possibly formed by,



Small  $C_4$  fractions, at rates not exceeding  $0.5 \times 10^{-3}$  cc. N.T.P./sec., were found by mass spectrometric analysis to contain at least 50% acetone while the rest could not be identified positively as butane. Higher hydrocarbons, i.e.,  $C_5$  and  $C_6$ , were not detected at all by the mass spectrometer.

From Table II it is evident that the  $k'_A/k_2^{1/2}$  and  $k''_A/k_2^{1/2}$  values agree reasonably well. A comparison of the  $k'_A$  and  $k''_A$  values with  $k'''_A$  (Table III and Fig. 1) also shows reasonable agreement, viz. 7.5, 5.5, and 8.5 kcal. respectively.

TABLE III  
PHOTOLYSIS OF ACETONE AND ETHYLENE (REF. TABLE I, a)

Temp., ° C.	$[(CH_3)_2CO]$	$[C_2H_4]$ init.	$[C_2H_4]$ fin.	$R_{C_2H_6}$	$R_{CH_4}$	$R_{CO}$	$R'_A$	$R''_A$	$\frac{k''_A}{k_2^{1/2}}$	$\frac{k'''_A}{k_2^{1/2}}$
	$\times 10^6$ M./cc.			$\times 10^3$ cc. N.T.P./sec.					$\times 10^{12}$ cm. <sup>3/2</sup> molecule <sup>-1/2</sup> sec. <sup>-1/2</sup>	
144	1.76	0.083	0.074	6.01	1.79	8.46	1.3	1.4	12	13
159	0.90	0.042	0.038	3.34	1.01	4.97	0.8		20	
177	1.76	0.083	0.068	4.70	3.59	9.49	2.2	1.8	25	20
204*	1.76	0.084	0.058	3.32	5.60	9.70	2.3	3.3	35	47
219	0.90	0.042	0.031	1.90	3.28	5.48	1.0	1.4	35	51
240	1.76	0.085	0.057	1.98	9.05	10.93	2.7	3.5	50	64
241	1.76	0.043	0.025	2.28	9.88	10.97	1.2	2.3	45	83
286	1.76	0.084	0.044	.94	13.15	12.40	3.0	5.1	88	153

\*Irradiation time = 3840 sec.

We may therefore state the value of  $E_A$  as  $E_A = 7.0 \pm 1.5$  kcal. It is noteworthy that changes in concentration of acetone and ethylene have no significant effect on the  $k''_A/k_2^{1/2}$  values. Furthermore, it can be seen that the addition of such small quantities of ethylene has no significant effect on the  $R_{CH_4}/R_{C_2H_6}^{1/2}$  ratios, thereby indicating that there are no complications due to abstraction of hydrogen atoms from ethylene.



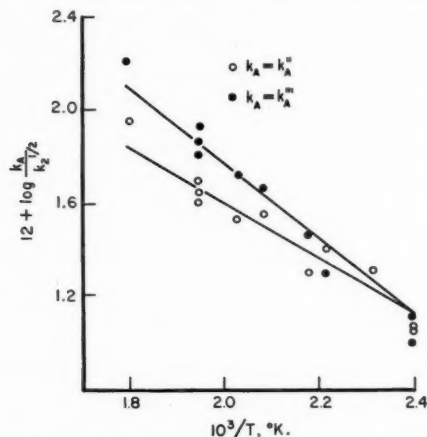


FIG. 1. Arrhenius plot for the addition of methyl radicals to ethylene.

### Propylene

The presence of propylene (Table IV) caused a small increase in the  $R_{C_2H_4}/R_{C_2H_6}^{1/2}$  ratios for the acetone photolysis which necessitated a correction for hydrogen abstraction in determining  $R'''_A$ . This correction was only about 10% of the rate of addition.

From Table IV and Fig. 2 it can be seen that up to 200° C. the  $k''_A/k_2^{1/2}$  and  $k'''_A/k_2^{1/2}$  values agree quite well, with the latter continuing the linear Arrhenius relationship while the former values fall off at higher temperatures. It may be concluded, therefore, that the activation energy for addition of methyl radicals to propylene is reasonably well established by the two methods to be approximately 6 kcal.

TABLE IV  
PHOTOLYSIS OF ACETONE AND PROPYLENE (REF. TABLE I, a)

Temp., °C.	$[(CH_3)_2CO]$	$[(C_3H_6)]$ init.	$[C_3H_6]$ fin.	$R_{C_2H_6}$	$R_{C_2H_4}$	$R_{CO}$	$R''_A$	$R'''_A$	$\frac{k''_A}{k_2^{1/2}}$	$\frac{k'''_A}{k_2^{1/2}}$
	$\times 10^6$ M./cc.			$\times 10^6$ cc. N.T.P./sec.					$\times 10^{12}$ cm. <sup>3/2</sup> molecule <sup>-1/2</sup> sec. <sup>-1/2</sup>	
144	1.76	0.166	0.150	6.32	1.90	9.58	2.5	1.9	12	9
160	0.9	0.166	0.148	2.68	1.17	5.15	2.2	2.0	16	15
177	1.76	0.085	0.069	6.00	4.34	11.36	1.8	1.8	18	18
189	1.76	0.083	0.067	4.75	5.09	10.30	2.0	1.9	23	22
189*	1.76	0.180	0.143	3.72	4.78	10.04	4.0	5.2	24	32
205	1.76	0.084	0.062	3.64	6.37	10.63	2.3	2.5	30	33
219	0.9	0.083	0.065	1.94	3.30	6.32	2.1	2.1	37	37
242	1.76	0.083	0.051	2.22	10.18	11.67	2.1	3.8	37	68
286	1.8	0.083	0.058	1.28	14.28	12.93	1.4	3.7	33	79

\* Used mercury cutoff for cell.

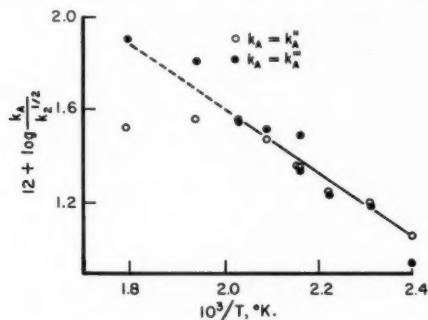


FIG. 2. Arrhenius plot for the addition of methyl radicals to propylene.

*Acetylene*

The products that were found in the various low temperature fractions were propylene, ethylene, and butene. Propylene, which was produced at about one third of the rate of addition (Table V), may be accounted for by abstraction of hydrogen atoms from acetone by propenyl radicals ( $\text{CH}_3\text{CH}=\text{CH}$ ) formed by addition of methyl radicals to acetylene. Butene was produced at a much smaller rate, less than 5% of the rate of addition, and therefore contributed very little to the loss of methyl radicals. The presence of ethylene in the  $\text{C}_2$  fraction was unexpected and is not readily explicable.

Two experiments were done at 270° C. with deuterated acetylene at concentrations of  $0.08 \times 10^{-6}$  mole/cc. and  $0.28 \times 10^{-6}$  mole/cc. acetylene in the presence of  $1.7 \times 10^{-6}$  mole/cc. acetone. Mass spectrometric analyses showed that both  $\text{CH}_3\text{D}$ , about 2% of the methane, and  $\text{C}_2\text{H}_5\text{D}$  were formed, thereby indicating an insignificant amount of abstraction of deuterium atoms by methyl radicals. Furthermore the absence of abstraction can be seen, as for ethylene, from the  $R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}^{1/2}$  ratios, which were hardly altered by the addition of acetylene to acetone.

From Table V and Fig. 3 it is evident that the  $k''_A/k_2^{1/2}$  and  $k'''_A/k_2^{1/2}$  values agree reasonably well. The Arrhenius plot is based on an average of the two

TABLE V  
PHOTOLYSIS OF ACETONE AND ACETYLENE (REF. TABLE I, a)

Temp., ° C.	$[(\text{CH}_3)_2\text{CO}]$	$[\text{C}_2\text{H}_2]$ init.	$[\text{C}_2\text{H}_2]$ fin.	$R_{\text{C}_2\text{H}_6}$	$R_{\text{CH}_4}$	$R_{\text{CO}}$	$R''_A$	$R'''_A$	$\frac{k''_A}{k_2^{1/2}}$	$\frac{k'''_A}{k_2^{1/2}}$
	$\times 10^6 \text{ M./cc.}$			$\times 10^6 \text{ cc. N.T.P./sec.}$				$\times 10^{12} \text{ cm.}^3/2 \text{ molecule}^{-1} \text{ sec.}^{-1/2}$		
144	1.76	0.085	0.061	6.04	1.74	9.39	2.9	3.1	28	31
175	0.9	0.042	0.037	3.09	1.45	5.40	1.4	1.4	40	40
177	1.76	0.085	0.059	4.10	3.56	10.07	4.3	3.3	52	40
199	0.9	0.083	0.059	2.06	2.02	5.97	3.3	3.1	63	57
205	1.76	0.085	0.057	3.44	6.50	11.16	3.7	3.6	52	51
219	0.9	0.042	0.029	1.82	3.14	5.76	1.7	1.7	73	72
241	1.76	0.085	0.039	1.81	9.84	12.91	5.0	5.9	113	131

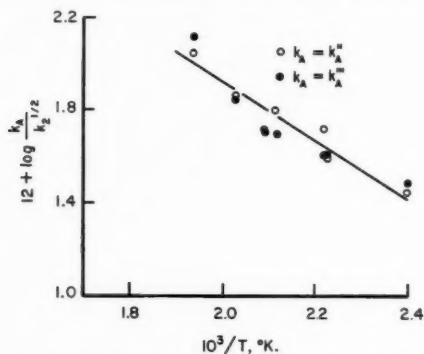


FIG. 3. Arrhenius plot for the addition of methyl radicals to acetylene.

values at each temperature, but if they are considered separately the difference in activation energies by the two methods is 1 kcal.

#### Butadiene

The experimental results for butadiene are shown in Table VI but the rate constants, which contain a term for the average concentration of unsaturated

TABLE VI  
PHOTOLYSIS OF ACETONE AND BUTADIENE (REF. TABLE I, b)

Temp., ° C.	$C_4H_6$ init. $\times 10^6$ M./cc.	$R_{C_2H_6}$	$R_{CH_4}$	$R_{CO}$	$R''_A$
		$\times 10^6$ cc. N.T.P./sec.			
164	0.018	6.18	2.88	10.12	1.7
164	0.019	6.08	2.94	9.98	1.6
164	0.039	4.78	2.61	9.92	4.4
180	0.019	5.37	4.04	10.39	2.1
180	0.038	4.99	3.87	10.97	3.9
200	0.018	3.72	5.67	9.61	1.4
200	0.035	3.04	5.17	9.41	2.9
236	0.019	2.18	9.45	10.17	1.3
236	0.036	1.82	8.61	9.95	2.6

Used mercury cutoff for cell.

hydrocarbon, could not be calculated directly since analyses for butadiene were not made at the end of the experiments. From the  $R_{CH_4}/R_{C_2H_6}^{1/2}$  ratios it can be seen that there was some hydrogen abstraction at the lower temperatures and none at the higher temperatures indicating that, at the higher temperatures, butadiene disappeared rapidly and almost completely. Therefore if the  $k''_A/k_2^{1/2}$  values are calculated on the assumption that no butadiene remained at the end of the experiments at the higher temperatures and that its rate of consumption was equal to  $R''_A$  at the lower temperatures, an activation energy of  $\sim 2.5$  kcal. is obtained for the addition reaction.

#### DISCUSSION

The activation energies and steric factors obtained for the addition of methyl radicals to the various hydrocarbons investigated are summarized in Table VII.

TABLE VII  
 ADDITION OF METHYL RADICALS TO UNSATURATED HYDROCARBONS

Hydro-carbon	$k_A/k_2^{1/2}$ at 200° C. $\times 10^{12}$ cm. <sup>3/2</sup> molecule <sup>-1/2</sup> sec. <sup>-1/2</sup>	$E_A - \frac{1}{2}E_2$ , kcal.	$\frac{P_A}{P_2^{1/2}} \times 10^4$
C <sub>2</sub> H <sub>4</sub>	29	7.0	5
C <sub>3</sub> H <sub>6</sub>	28	6.0	3
C <sub>3</sub> H <sub>2</sub>	60	5.5	5
C <sub>4</sub> H <sub>6</sub>	~110	~2.5	0.3

One striking feature of these results is the similarity of the values obtained for addition to ethylene, propylene, and acetylene.

Raal, Danby, and Hinshelwood (2, 7, 8) studied the addition of methyl radicals to unsaturated hydrocarbons, the methyl radicals being produced by the photolysis of acetaldehyde. According to their kinetic scheme they found that the ratios of the rate constants of addition to that of abstraction of hydrogen, by methyl radicals from acetaldehyde were essentially similar for the series of hydrocarbons investigated, that for ethylene being lower than the others. For ethylene, they also determined the difference in activation energies of the two reactions, from which 6.8 kcal. was obtained for the addition reaction by assuming 9.7 kcal. for the abstraction reaction. However, if the values of 7.5 kcal. and  $\sim 10^{-3}$  for the activation energy and steric factor for the latter reaction (9) are applied to their data on ethylene an activation energy of 4.6 kcal. and steric factor of  $\sim 10^{-5}$  are obtained which are at least of the same order as the results of the present investigation.

The activation energy of chain propagation in the polymerization of butadiene induced by methyl radicals has been found to be 5.4 kcal. by Volman and Graven (10), who considered it as the activation energy for the addition of methyl radicals to butadiene. This value is in poor agreement with the value of 2.5 kcal. obtained here for this reaction, but it may not correspond to the addition reaction.

The difference between the activation energies of the addition reaction and its back reaction, or decomposition of the free radical product, should be equal to the heat of the reaction. Three independent investigations (1, 3, 6) agree on an activation energy of  $\sim 20$  kcal. for the decomposition of propyl radicals to methyl radicals and ethylene. This activation energy is, however, about 3 kcal. lower than the lower limit of the heat of the reaction, a discrepancy which has been pointed out. With the present value of the activation energy of the addition reaction, the discrepancy is about 10 kcal. The values for the decomposition of the propyl radical should, therefore, be regarded with some suspicion.

#### ACKNOWLEDGMENT

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# THE VISCOSITY OF GASES AND THE THEORY OF CORRESPONDING STATES<sup>1</sup>

By E. WHALLEY

## ABSTRACT

The viscosity of gases is examined using the theory of corresponding states. The curve of reduced viscosity plotted against reduced temperature is compared with the theoretical curves obtained for several intermolecular potentials. The approximate Sutherland equation gives the best fit and it is suggested that this be used to extrapolate viscosities to high temperatures where experimental data are not available. The reduced viscosity - reduced temperature plot can be used for estimating the viscosities of simple gases from critical data, or critical data from the viscosities.

## INTRODUCTION

Several authors have shown (6, 17) that if one makes certain assumptions the reduced low pressure transport properties of monatomic gases obeying classical statistics should be universal functions of the reduced temperature. The arguments were based on the principle of corresponding states discussed by Pitzer (16) and Guggenheim (3, 4) and on the kinetic theory of gases, and need not be detailed again. The validity of the arguments depends on several assumptions, the most restrictive of which is that the potential  $\phi(r)$  of two molecules separated by a distance  $r$  is given by an equation of the form

$$[1] \quad \phi(r) = \epsilon f(r_0/r),$$

where  $\epsilon$  is an energy,  $r_0$  a distance, and  $f$  a universal function. Some authors have preferred to use the molecular quantities  $\epsilon$  and  $r_0$ , where  $\epsilon$  is the depth of the minimum of the potential energy curve and  $r_0$  is the value of  $r$  for either  $\phi = 0$  or  $\phi = \epsilon$ , to reduce the properties considered. However, to apply the reduced equations,  $\epsilon$  and  $r_0$  have to be evaluated using an assumed form of  $f$ , and the Lennard-Jones 12:6 potential is frequently used. It is more general practice to assume that  $\epsilon$  is proportional to the critical temperature  $T_c$  and that  $r_0^3$  is proportional to the critical volume  $V_c$  and to use  $T_c$  and  $V_c$  as reducing quantities. The advantage of this procedure is that it is independent of the form of  $f$  and uses macroscopic quantities only. In this paper I use the latter assumption.

The reduced transport coefficients are (6, 17)  $\eta V_c^{2/3}/\sqrt{MT}$ ,  $\lambda V_c^{2/3}\sqrt{M/T}$ ,  $D_{12} V_c^{2/3} P/T^{3/2}[(M_1 + M_2)/M_1 M_2]^{1/2}$ , and  $R_T$ , where  $\eta$  is the viscosity,  $\lambda$  the thermal conductivity,  $D_{12}$  the coefficient of mutual diffusion of molecules 1 and 2,  $R_T$  the thermal diffusion ratio for isotopic mixtures,  $M$  the molecular weight,  $T$  the temperature, and  $P$  the pressure. Each of these quantities should be a universal function of the reduced temperature  $T_r = T/T_c$  for gases which obey the principle of corresponding states.

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There are insufficient data on monatomic gases to test the reduced thermal conductivity. The conductivity of other gases is complicated by exchange between translational and internal energy. Rowlinson and Townley (17) have shown that the reduced diffusion coefficients plotted against reduced temperature do not fall on a good line, possibly because of fairly large errors in the experimental measurements. A graph of  $\bar{R}_T$  vs.  $T_r$  was prepared, but showed a similar scatter to the one for concentration diffusion. The discussion is therefore confined to the viscosity.

#### REDUCED VISCOSITY CURVE

It appears to have been first suggested by Onnes (15) that  $\eta V_c^{2/3}/\sqrt{MT}$  should be a universal function of  $T_r$ . Several authors (2, 17, 18, 21) have verified this by plotting the above form of the reduced viscosity or a related one and obtained good curves. The published graphs have, however, been

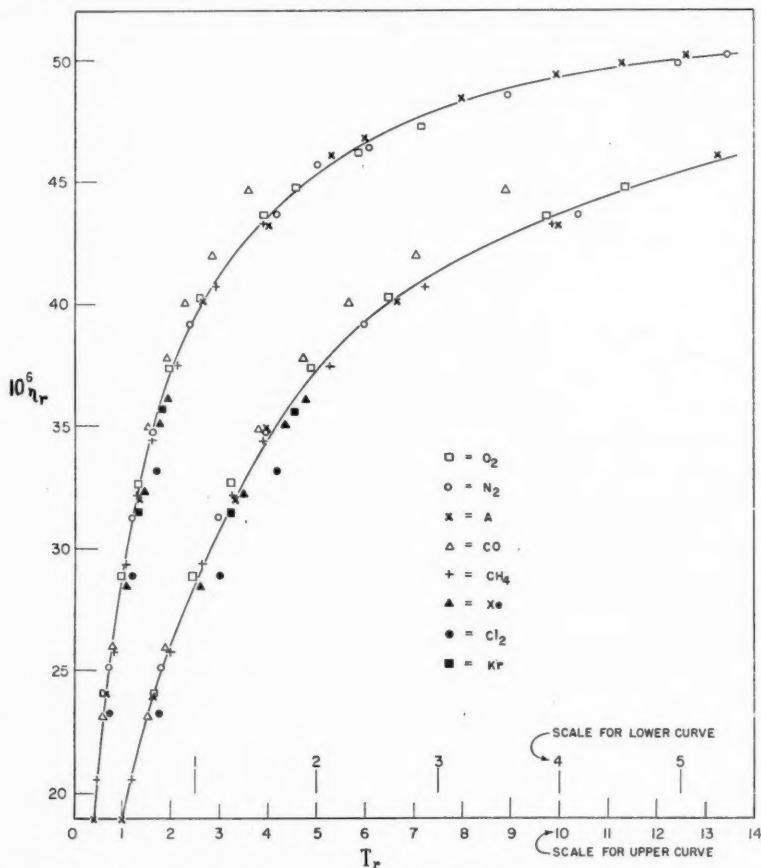


FIG. 1. Reduced viscosity against reduced temperature for several gases.



confined to comparatively low temperatures. Fig. 1 is a graph of this function over a fairly wide range of  $T$ , using the smoothed viscosity data obtained for another paper (24) and the critical constants collected by Guggenheim (3, 4), except that for xenon the data of Weinberger and Schneider (22) were used. The viscosity data for methane (7, 20), carbon monoxide (19), krypton and xenon (11) were obtained by smoothing the data in the literature.

Neon does not fit the normal curve and hydrogen and helium deviate much further. These deviations are due at least partly to quantum effects. The use of "corrected" critical constants, i.e. those which would be obtained if there were no quantum effects, as suggested by Guggenheim and McGlashan (4), did not bring hydrogen, helium, and neon into line with the other gases, nor was it found possible to choose empirical values of the "critical constants" which would bring them into line. Carbon monoxide falls a little above the curve for the remaining gases, probably owing to its small dipole moment.

#### COMPARISON WITH THEORY

Since the reduced viscosities of many gases fall quite close to one curve, it seems likely that the true potential of these gases approximates closely to the form of Equation [1], and by comparing the experimental and theoretical reduced viscosity curves one can examine the degree of fit with the viscosity obtained with various forms of  $f$ .

The general theory of viscosity (1) gives the equation

$$[2] \quad 10^6 \eta = 26.693 \sqrt{MT} r_0^{-2} f_n / \Omega(2,2),$$

where  $f_n$  and  $\Omega(2,2)$  are functions of  $kT/\epsilon$  to be worked out for each potential, and  $r_0$  is in angstroms.

##### (1) The Sutherland Potential

For this potential

$$[3] \quad \begin{aligned} &\text{when } r < r_0, \quad f = \infty, \\ &\text{when } r > r_0, \quad f = (r_0/r)^n, \end{aligned}$$

and  $\epsilon$  is the depth of the potential energy minimum. The values of  $f_n$  and  $\Omega(2,2)$  have been worked out for values of  $n$  of 4 (5) and 6 (10) only. To a first approximation, neglecting second and higher powers of  $\epsilon/kT$ , Equation [2] reduces to the Sutherland equation

$$[4] \quad 10^6 \eta = 26.693 (MT)^{1/2} r_0^{-2} (1 + S/T)^{-1},$$

where  $S$  is Sutherland's constant and is proportional to  $\epsilon$ . Equation [4] is not a good approximation to Equation [2] except at high temperatures when  $S/T$  is small, but it is simple and easy to apply and has been very frequently used in correlating viscosity data. We shall see later that Equation [4] provides the best representation of the reduced viscosity curve of any of those considered.

We first consider Equation [2]. We assume

$$[5] \quad \begin{aligned} V_c &= \beta N r_0^3 10^{-24}, \\ T_c &= \gamma \epsilon / k, \end{aligned}$$

where  $N$  is the Avogadro number, and obtain by substituting into Equation [2]

$$[6] \quad 10^6 \eta_r = 10^6 \eta V_c^{2/3} / \sqrt{MT} = 18.759 \beta^{2/3} f_\eta / \Omega(2,2).$$

It is generally accepted that  $n = 6$  is the best simple representation of the attractive potential. I have therefore not discussed the potential  $n = 4$ . Using the tables of  $f_\eta$  and  $\Omega(2,2)$  given by Kotani for  $n = 6$  and solving the two simultaneous equations obtained from the values of  $\eta_r$  at  $T_r = 1$  and 10, i.e. forcing Equation [6] to fit the experimental curve at  $T_r = 1$  and 10, we solve for  $\beta$  and  $\gamma$ . The theoretical curve can then be calculated. It is not plotted in Fig. 2 since it is of little practical or theoretical importance and would confuse the graph. Up to  $T_r = 3$  it follows roughly curve 5 and above about  $T_r = 10$  it is indistinguishable from curve 2.

Equation [4] is of more practical value. We assume (12) that the reduced Sutherland constant

$$S_r = S/T_c$$

is constant for all gases; since  $S \propto \epsilon$ , this is equivalent to assuming that  $T_c \propto \epsilon$ . Also we assume that  $r_0$  is related to the critical volume by the equation

$$V_c = \beta N r_0^3 10^{-24}.$$

Inserting these in Equation [4] and rearranging, we obtain

$$[7] \quad 10^6 \eta_r = 18.759 \beta^{2/3} / (1 + S_r/T_r).$$

By fitting Equation [7] to the curve of Fig. 1 at  $T_r = 1$  and 10, we obtain

$$[8] \quad \begin{aligned} \beta &= 2.006, \\ S_r &= 0.8385. \end{aligned}$$

This value of  $S_r$  is close to the value of 0.8 used by Light and Stechert (12). The curve obtained using Equations [7] and [8] is compared with the experimental curve in Fig. 2.

## (2) 12 : 6 Potential

For this potential

$$f = 4 \{ (r_0/r)^{12} - (r_0/r)^6 \},$$

where  $r_0$  is the low velocity collision diameter and  $\epsilon$  is the depth of the potential energy minimum.  $f_\eta$  and  $\Omega(2,2)$  are tabulated by Hirschfelder *et al.* (6). We assume Equations [5] and obtain

$$[9] \quad 10^6 \eta_r = 18.759 \beta^{2/3} f_\eta / \Omega(2,2).$$

By solving graphically the simultaneous equations [9] at  $T_r = 1$  and 10, we obtain

$$[10] \quad \begin{aligned} \beta &= 2.784, \\ \gamma &= 1.540. \end{aligned}$$

By fitting viscosity data of a number of gases to the 12 : 6 potential, usually at moderate temperatures only, Hirschfelder *et al.* obtained  $\beta = 3.1$ ,  $\gamma = 1.28$ .

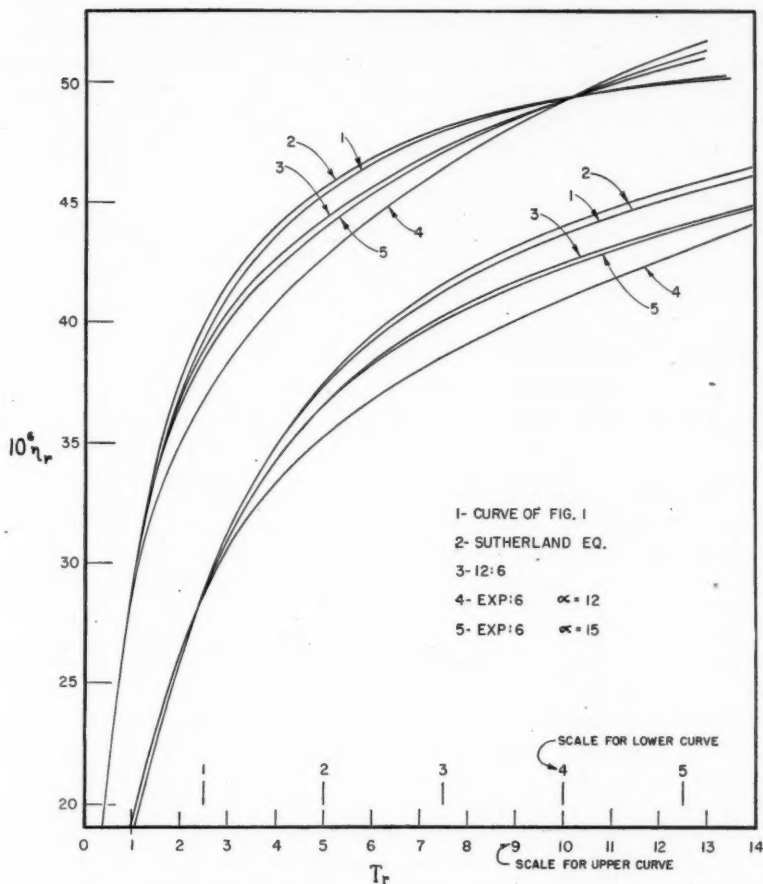


FIG. 2. Comparison of experimental and theoretical reduced viscosity curves.

Guggenheim and McGlashan fitted the reduced second virial coefficient curve and obtained  $\beta = 2.836$ ,  $\gamma = 1.28$ . The calculated  $\eta_r$  curve is compared with the experimental curve in Fig. 2.

### (3) Exponential : 6 Potential

Very recently Mason (13) has given a table of the transport integrals for a potential of the form

$$f = \frac{1}{1 - 6/\alpha} \left\{ \frac{6}{\alpha} \exp(1 - r/r_m) - \left( \frac{r_m}{r} \right)^6 \right\},$$

where  $r_m$  is the position of the potential energy minimum,  $\alpha$  is a measure of the steepness of the repulsive potential, and  $\epsilon$  is the depth of the potential energy minimum. For this potential

$$[11] \quad 10^6 \eta_r = 26.693 \sqrt{MT} r_m^{-2} f_\eta / \Omega(2,2),$$

where  $r_m$  is in angstroms and  $f_\eta$  and  $\Omega(2,2)$  are functions of  $kT/\epsilon$  and  $\alpha$  only. They are tabulated for values of  $\alpha$  of 12, 13, 14, and 15. We assume the relations [5] and fit the reduced viscosity as before for  $\alpha = 12$  and for  $\alpha = 15$ . The curves are compared with the experimental curve in Fig. 2. For  $\alpha = 12$  we find

$$\begin{aligned} \beta &= 1.510, \\ \gamma &= 2.409. \end{aligned}$$

For  $\alpha = 15$  we find

$$\begin{aligned} \beta &= 1.858, \\ \gamma &= 1.536. \end{aligned}$$

#### DISCUSSION

For the gases considered the approximate Sutherland equation provides a better fit over a wide temperature range than the "exact" Sutherland, 12 : 6 or exp : 6 potentials. It has been pointed out several times (8, 9, 23, 24) that a 12 : 6 potential is not good for the viscosity of many gases at higher temperatures. Kihara and Kotani showed that for nitrogen and methane the accurate Sutherland potential is better than the 12 : 6. The approximate Sutherland equation is better still. It was shown recently (23, 24) that the 12 : 6 potential does not give a good representation of the viscosity of most gases at high temperatures, e.g. for nitrogen it was impossible to obtain any 12 : 6 parameters to fit the viscosity above about 570°K., whereas the Sutherland equation could be used over the whole range of 80–1800°K. with only a few per cent change in  $S$ . It should be remarked however that this conclusion does not hold for all the simple gases. The viscosity of neon (24) is quite well represented by a 12 : 6 potential over the temperature range 80–1100°K. for which data are available. The viscosity of helium and hydrogen (14) is well described by an exp : 6 potential.

If any conclusions about the shape of the potential energy curve which will give the best fit to the viscosity data can be drawn from this comparison it is that the repulsive energy should be steeper than that of the exp : 6,  $\alpha = 15$ . This does not necessarily indicate that the true repulsive energy should be steeper. Undoubtedly a better fit to the observed data could be obtained with a modified Sutherland equation. Keyes (8) used the equation

$$10^6 \eta = \frac{a_0 \sqrt{T}}{1 + a\tau/10^{a_1\tau}}$$

where  $\tau = T^{-1}$ ,  $a_0$ ,  $a$ , and  $a_1$  are constants to correlate successfully the viscosities of a number of simple gases over a wide temperature range. At higher temperatures this reduces to the Sutherland equation. Simple modifications involving the substitution of  $1 + S_r/T_r + S_r^2/T_r^2$  or  $\exp(1 + S_r/T_r) - 1$  for  $1 + S_r/T_r$  gave a worse fit than Equation [7].

The curve of Fig. 1 is very useful in providing a means of estimating the viscosity of a simple gas when only critical data or scanty viscosity data are available. Alternatively it is possible to obtain values of the critical volume

and temperature from viscosity data, to enable one to make use of other reduced curves for estimating rough values of gas properties.

One should be able to make a similar plot for the viscosity of simple liquids, but a few graphs showed fairly considerable deviations and the subject was not pursued further.

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# MICROCALORIMETRIC STUDIES OF POLYVINYL ACETATE SOLUTIONS<sup>1</sup>

BY HUBERT DAOUST<sup>2</sup> AND MARCEL RINFRET

## ABSTRACT

A relation between intrinsic viscosity and the sign of heat of mixing of a linear polymer in different solvents has been predicted by Alfrey, Bartovics, and Mark. To verify this, the intrinsic viscosities and heats of mixing at one concentration for two samples of polyvinyl acetate in six solvents were determined. The heats of mixing have been measured with a Tian-Calvet microcalorimeter especially designed for slow processes and having a sensitivity of one thousandth of a calorie per hour. The results generally agree with the above prediction. Furthermore, the heats of mixing of two fractions of polyvinyl acetate in three solvents have been measured over a range of low concentrations to study the behavior of the quantity  $B$  from the theory of van Laar, Scatchard, and Hildebrand on energy of mixing of nonelectrolytes. It was found that  $B$  goes through a minimum at low concentrations when the mixing process is exothermic. This effect may be explained by the existence of a critical concentration below which entanglement between macromolecules ceases. For a poor solvent,  $B$  seems to be constant at high dilution.

## INTRODUCTION

When a linear polymer such as polyvinyl acetate has a high molecular weight, it usually assumes a solid form of an amorphous or slightly crystalline structure. Thus, a solid high polymer is far from being a perfect solid and is often considered as a very viscous liquid (10). A solution of linear and nonelectrolytic macromolecules in an organic solvent is the limiting case of solutions of nonelectrolytes of different molecular dimensions. These solutions deviate strongly from ideal behavior and the mixing process is often accompanied by a thermal effect.

Van Laar, Scatchard, and Hildebrand have worked out a general theory on total energy of mixing  $\Delta E_M$  for two nonpolar nonelectrolytic liquids (9). Since the volume change on mixing  $\Delta V_M$  is negligible for very dilute polymer solutions, then, according to this theory,

$$[1] \quad \Delta H_M \simeq \Delta E_M = V_M B \Phi (1 - \Phi),$$

$V_M$  being the total volume of mixture, and  $\Phi$  the volume fraction of the solute.

The quantity  $B$  is a parameter characterizing the net heat of interaction for a given pair of nonelectrolytes (8) which theoretically is independent of concentration and varies with temperature. If only dispersion forces are present it may be given as (9)

$$[2] \quad B = (\delta_1 - \delta_2)^2$$

where  $\delta_1$  and  $\delta_2$  are solubility parameters. Therefore according to [2],  $\Delta H_M$  is

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always positive or zero, i.e. the mixing is an endothermic or an athermic process.

However when there is specific interaction between two species in solution the value of  $B$  is not given by [2] but becomes more complex and often negative. Equation [1] is still applicable but  $\Delta H_M$  can be negative.

Based on theoretical considerations of the shape of polymers in solution and intrinsic viscosity, Alfrey, Bartovics, and Mark (2) have predicted that in an energetically unfavorable solvent, the polymer segments will attract each other and will reduce the polymer-solvent contacts. The intrinsic viscosity should then be low and the mixing process should be endothermic, i.e.  $\Delta H_M > 0$ . However if a solvent is energetically more favorable, the intrinsic viscosity should be higher and the mixing process, exothermic. According to their investigations and those of others (1,7) on the viscosity, at various temperatures, of linear polymers in different solvents, these predictions were essentially correct. Here the values of  $B$  along with the intrinsic viscosities were determined at one low concentration for two samples of polyvinyl acetate in six solvents to verify previous work on viscosity behavior of the same polymer in the same solvents (6) and the predictions of Alfrey, Bartovics, and Mark. Furthermore, the variation of  $B$  was studied in the low concentration range for one poor and for two good solvents of polyvinyl acetate.

#### EXPERIMENTAL

An unfractionated sample of polyvinyl acetate of average molecular weight 145,000 was provided by Bakelite Corp. Fractions of the same polymer were obtained through the kindness of Dr. Sheffer of the Defence Research Board of Canada. The samples of polymer were kept under vacuum over phosphoric anhydride. The solvents used were rectified through a high efficiency distilling column (13) and stored over "Drierite".

Intrinsic viscosities were measured by a method described in a previous paper (6). Flow time for benzene at 25°C. was 128.7 sec. and the concentration range studied extended from 0.2 to 1.0 gm. per 100 ml.

The heats of mixing were measured with a conduction microcalorimetric system which was originally designed by Tian (16) for measuring very small quantities of heat evolved in very slow phenomena. This apparatus was further modified by Calvet (4) by the introduction of a differential system which gave higher sensitivity and a greatly lengthened period of operation (one week or more).

The microcalorimeter used here was of the Calvet modification type and comprised two cells, each having 144 iron-constantan thermocouples, connected differentially through a high sensitivity galvanometer and a switching arrangement providing three sensitivities.

As shown by the Tian equation (16) the measurement of heat evolved is made by integrating the area under the curve of galvanometer deflections versus time. These deflections were recorded by a photographic drum or by a Beckman "Photopen" photoelectric light spot follower described by Pompeo and Penther (12). The areas were measured with a planimeter. Calibration



was effected by passing a known current through a manganin resistor immersed in a liquid in the calorimeter cell. Results of calibrations for a paper speed of 10.16 cm. per hour are given in Table I. The accuracy was limited to  $\pm 0.5\%$

TABLE I

Sensitivity in use	Calibration factor in cal. per cm. <sup>2</sup>
Low	0.0870 $\pm$ .0004
Medium	0.0324 $\pm$ .00015
High	0.00446 $\pm$ .00002

by the reproducibility of galvanometer deflections in the range of relatively high heat exchanges, i.e. 0.1, 0.8, and 2.0 calories per hour at the high, medium, and low sensitivities respectively. For still smaller evolutions of heat the limiting factor lies in the determination of the area under the deflection-time curve which can be measured to  $\pm 0.02$  cm.<sup>2</sup>. Thus it can be seen from Table IV that for the smallest value of  $\Delta H_M$  of  $-0.020$  cal., which corresponds at high sensitivity to 4.5 cm.<sup>2</sup>, 0.02 cm.<sup>2</sup> contributes an error of  $\pm 0.5\%$ . This coupled with the possible galvanometer error gives a maximum error of 1%. For higher  $\Delta H$ 's the error would tend towards 0.5%.

The method used for mixing solvent and solid polymer has been described by Calvet (3) and a new method has been developed when the polymer is not a compact solid (5). The volume of solvent varied between 6 and 8 ml. and the mass of polymer used was from 8 to 224 mgm.

## RESULTS

Table II shows the intrinsic viscosities along with the quantities  $B$  calculated from equation [1] for a fractionated sample of polyvinyl acetate (M.W. 135,000)

TABLE II  
HEAT OF MIXING AND INTRINSIC VISCOSITY OF POLYVINYL ACETATE IN  
VARIOUS SOLVENTS

Solvents	$\Delta H_M$	$B$ , cal. per ml.	$[\eta]$
Chloroform	-0.885	-12.5	1.06
Ethylene chloride	-0.252	-3.7 <sub>4</sub>	0.91 <sub>7</sub>
Chlorobenzene	-0.092	-1.5 <sub>6</sub>	0.76 <sub>7</sub>
Benzene	0.046	0.642	0.71 <sub>3</sub>
Toluene	0.119	1.53	0.50 <sub>9</sub>
Methanol	1.04 <sub>6</sub>	7.9 <sub>4</sub>	0.44 <sub>8</sub>

at 25°C. in six solvents. The values of  $B$  are given for one concentration only (1 gram of polymer in 1 mole of solvent). The densities of the solvents have been calculated from the International Critical Tables and the density of polyvinyl acetate has been taken as 1.17 (11). The relation between  $B$  and  $[\eta]$  is illustrated by the curve in Fig. 1.

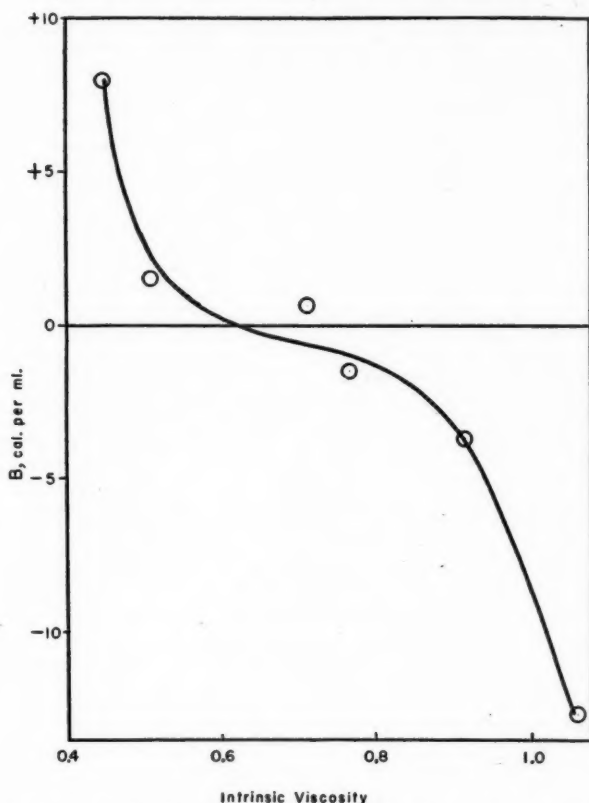


FIG. 1. Variation of parameter  $B$  with the intrinsic viscosity for polyvinyl acetate in different solvents.

The results of the study of the parameter  $B$  in the low concentration range are given in Tables III, IV, and V for a fraction of polyvinyl acetate (M.W. 85,000) in methanol and ethylene chloride and for another fraction (M.W. 58,000) in *s*-tetrachloroethane. Figs. 2-7 show the curves obtained from these

TABLE III  
HEATS OF MIXING POLYVINYL ACETATE IN METHANOL AT 25.2°C.  
(M.W. 85,000, FRACTIONATED)

$\Phi$	$\Delta H_M$ , cal.	$V_M$ , ml.	$\Delta H_M/V_M$	$B$ , cal. per ml.
.002	0.123	7.343	.017	8.4 <sub>0</sub>
.004	0.213	6.480	.033	8.2 <sub>1</sub>
.009	0.54 <sub>1</sub>	7.127	.076	8.5 <sub>1</sub>
.012	0.74 <sub>9</sub>	7.469	.100	8.4 <sub>1</sub>
.019	0.92 <sub>9</sub>	6.356	.146	7.8 <sub>4</sub>
.021	1.18	7.311	.162	7.8 <sub>5</sub>
.030	1.38	6.271	.220	7.5 <sub>8</sub>

TABLE IV  
HEATS OF MIXING POLYVINYL ACETATE IN ETHYLENE CHLORIDE AT 25.2°C.  
(M.W. 85,000, FRACTIONATED)

$\Phi$	$\Delta H_M$ , cal.	$V_M$ , ml.	$\Delta H_M/V_M$	$B$ , cal. per ml.
.001	-.020	6.436	-.003 <sub>1</sub>	-3.1 <sub>0</sub>
.002	-.044	6.920	-.006 <sub>4</sub>	-3.2 <sub>0</sub>
.003	-.079	7.565	-.010 <sub>4</sub>	-3.4 <sub>7</sub>
.004	-.115	7.194	-.016 <sub>0</sub>	-4.0 <sub>0</sub>
.006	-.167	7.215	-.023 <sub>1</sub>	-3.8 <sub>5</sub>
.009	-.192	6.664	-.029 <sub>0</sub>	-3.2 <sub>4</sub>
.011	-.220	6.482	-.034 <sub>0</sub>	-3.1 <sub>1</sub>
.013	-.252	6.391	-.039 <sub>4</sub>	-3.0 <sub>9</sub>
.016	-.240	6.430	-.037 <sub>2</sub>	-3.0 <sub>8</sub>

TABLE V  
HEATS OF MIXING OF POLYVINYL ACETATE IN S-TETRACHLOROETHANE AT 25.2°C.  
(M.W. 58,000, FRACTIONATED)

$\Phi$	$\Delta H_M$ , cal.	$V_M$ , ml.	$\Delta H_M/V_M$	$B$ , cal. per ml.
.0009	-0.110	7.920	-.013 <sub>9</sub>	-15.3
.0013	-0.149	6.973	-.021 <sub>4</sub>	-16.5
.0016	-0.264	6.869	-.038 <sub>4</sub>	-24.0
.0048	-0.682	7.492	-.091 <sub>0</sub>	-19.0
.0065	-0.852	6.783	-.126	-19.6
.0081	-1.07	7.339	-.146	-18.3

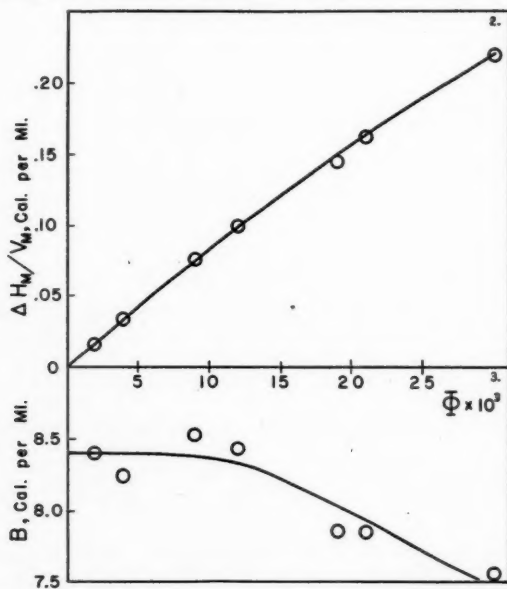


FIG. 2. Heats of mixing of polyvinyl acetate (M.W. 85,000, fractionated) in methanol at 25.2°C.

FIG. 3. Variation of  $B$  with  $\Phi$  for polyvinyl acetate (M.W. 85,000, fractionated) in methanol at 25.2°C.

results. In Figs. 2, 4, and 6 we have used  $\Phi$  instead of  $\Phi(1 - \Phi)$  because in this range of concentration  $\Phi \simeq \Phi(1 - \Phi)$ .

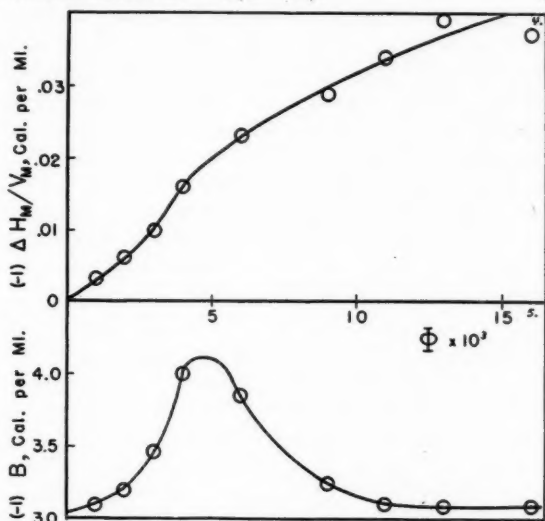


FIG. 4. Heats of mixing of polyvinyl acetate (M.W. 85,000, fractionated) in ethylene chloride at 25.2°C.

FIG. 5. Variation of  $B$  with  $\Phi$  for polyvinyl acetate (M.W. 85,000, fractionated) in ethylene chloride at 25.2°C.

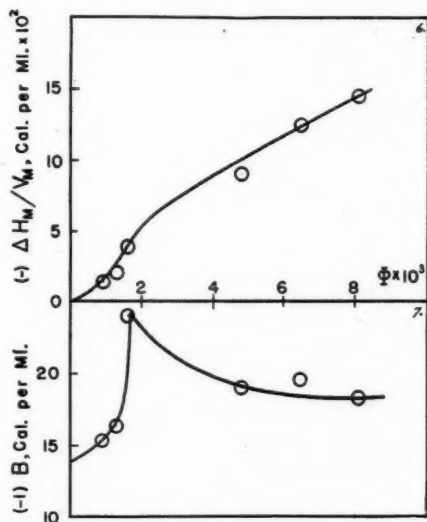


FIG. 6. Heats of mixing of polyvinyl acetate (M.W. 58,000, fractionated) in *s*-tetrachloroethane at 25.2°C.

FIG. 7. Variation of  $B$  with  $\Phi$  for polyvinyl acetate (M.W. 58,000, fractionated) in *s*-tetrachloroethane at 25.2°C.

## DISCUSSION

It has been shown here experimentally that the relation between the heat of mixing and the intrinsic viscosity predicted by Alfrey, Bartovics, and Mark is correct. Referring to Table II, it can be seen that for "acidic" solvents (in the sense of Lewis' theory), such as chloroform, ethylene chloride, and chlorobenzene, the mixing process is exothermic. A negative heat of mixing is usually explained by solvation, i.e. there is a strong attraction between solvent and solute. Molecules of acidic solvent are fixed to the polymeric chain by the "basic" carbonyl groups in polyvinyl acetate; thus the contacts between segments in the chain are hindered and the macromolecule assumes a less compact form causing high values of the intrinsic viscosity. In a neutral solvent such as benzene,  $\Delta H_M$  is very small, indicating that the values of the solubility parameters of the two substances are very close (6). In toluene and in methanol, which is a "basic" solvent,  $\Delta H_M$  is positive and the values for  $[\eta]$  are lower. This is explained by the more compact form of the polymer molecules in solution in these solvents. Results very similar to those in Table II were obtained for the unfractionated sample of polyvinyl acetate of average molecular weight 145,000 both at 25 and 35°C.

The results obtained on the heats of mixing of polyvinyl acetate in methanol at different concentrations (Table III, Figs. 2 and 3) show that when  $\Delta H_M$  is positive the theory of Van Laar, Scatchard, and Hildebrand holds at high dilutions, i.e. parameter  $B$  is constant. However, as the concentration increases,  $B$  decreases. When the mixing is exothermic the results are rather surprising as the curves (Figs. 4 and 6) possess an inflection point in the low concentration region. This particular behavior was established by repeating the experiments several times with utmost care to avoid any fortuitous error. For ethylene chloride, Table IV and Fig. 5 show that the absolute value of  $B$  increases to a maximum at  $\Phi = 0.45 \times 10^{-2}$ . This phenomenon is also illustrated by the inflection point in the curve of the heats of mixing per ml. vs.  $\Phi$  (Fig. 4). Similar results were obtained with *s*-tetrachloroethane (Table V, Figs. 6 and 7), but the maximum absolute value for  $B$  occurs here at  $\Phi = 0.17 \times 10^{-2}$ . Apparently there is a critical concentration (14) in a given polymer-solvent system for exothermic mixing at which  $B$  goes through a minimum value.

Streeter and Boyer (15) also observed a critical effect on the viscosity of very dilute solutions of polystyrene in toluene. They found that reduced viscosity decreases linearly as concentration is lowered from 1.0 to 0.1 gm. per 100 ml. and then increases with further dilution. They have accounted for the phenomenon by the fact that at medium and high concentration, polymer molecules are closely packed together and the solution is continuous. But if the mixture is diluted a critical concentration is reached at which the macromolecules do not touch each other and the solution becomes discontinuous. In other words at very low concentration, the polymer molecules are free in their movements and at high concentration they are entangled. The concentration region through which  $B$  varies rapidly apparently corresponds to the change in structure of the polymer in solution.

## ACKNOWLEDGMENTS

The authors wish to express their appreciation to Prof. Edouard Calvet of the University of Marseille, who supervised part of the construction of these microcalorimeters both at Marseille and at Montreal, and to the National Research Council of Canada which provided funds for two microcalorimeters in the Department of Chemistry.

Thanks are also due to Prof. Henri Prat, of the Department of Biology, who has generously let us use his microcalorimeter for part of this investigation; to C. E. Pion, our departmental mechanic, for his untiring efforts in the construction of these microcalorimeters; to the Associate Committee for Synthetic Rubber Research of the National Research Council which has contributed by the award of research grants and summer assistances.

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## ORGANIC DEUTERIUM COMPOUNDS

### XI. SYNTHESIS OF 1-CHLORO-1-ALKYNES AND 1-CHLORO-1-PROPYNE- $d_3$ <sup>1</sup>

BY A. T. MORSE AND L. C. LEITCH

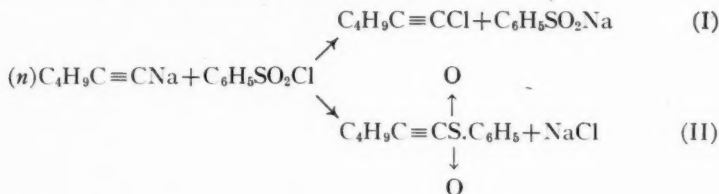
#### ABSTRACT

Dehydrohalogenation of *cis*-1,2-dichloro-1-alkenes,  $RCCl=CHCl$ , with potassium hydroxide in butanol has been used to prepare a number of new 1-chloro-1-alkynes, viz. 1-chloro-1-propyne- $d_3$ , 1-chloro-1-propyne, 1-chloro-1-butyne, and 1-chloro-1-pentyne in good yields. The last three compounds were also prepared by chlorination of 1-propyne, 1-butyne, and 1-pentyne with sodium hypochlorite.

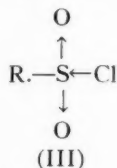
#### INTRODUCTION

The synthesis of several deuterated organic compounds of potential use in molecular spectroscopy has been reported in previous papers of this series (9, 10, 11). We have now synthesized normal and deuterated 1-chloro-1-propyne for further investigations in this field, which will be reported in this journal in a separate paper by Bernstein and Davidson (1).

As a class, the 1-chloro-1-alkynes have not been studied as extensively as other chlorinated hydrocarbons. In 1931, Truchet (18) obtained 1-chloro-1-hexyne (I) from benzenesulphonyl chloride and the sodium derivative of hexyne-1 instead of the expected sulphone (II).



This result is not surprising in view of the charge distribution between the sulphur and chlorine atoms in sulphonyl chlorides (III).



1-Hexyne, 1-octyne, and 1-nonyne reacted similarly. These chloroalkynes were later prepared by the same method by Pflaum and Wenzke (15) for dipole moment measurements. Cleveland, Taufen, and Murray (3) failed to obtain

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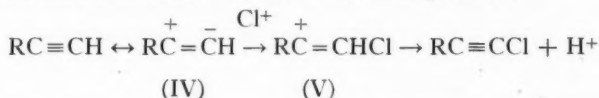


1-chloro-1-propyne from sodium methyl acetylide but an impure product, b.p. 37 to 41°C. was isolated in low yield using the magnesium derivative. In the present work, 1-chloro-1-propyne was actually obtained by Truchet's method but only in 10% yield; no improvement was observed using *p*-toluene-sulphonyl chloride.

Another synthesis of 1-chloro-1-alkynes was reported by McCusker and Vogt (13). These authors prepared the potassium derivative of 1-heptyne in the usual manner and chlorinated a suspension of the solid in ether at -70°C. The yield of 1-chloro-1-heptyne was good, but the rate of adding the chlorine was an important factor affecting the yield. This method appeared unpromising to us and was not tried. Chlorination of the lithium derivative, however, might be advantageous.

According to Strauss, Kollek, and Hauptmann (17), the methine or acetylenic hydrogen is replaced by bromine when heptyne-1 is shaken with alkali hypobromite; the reaction with hypochlorite was reported to be too slow to make this method a useful preparative route to 1-chloro-1-alkynes. However, vinylacetylene is reported to give 60 to 65% yields of 1-chloro-3-butene-1-yne when shaken at 0°C. with aqueous sodium hypochlorite for 16 hr. (8). There is also a reference to the chlorination of the methine hydrogen in propargyl alcohol by aqueous sodium hypochlorite by Copenhaver and Bigelow (4). In the present work, it was found that propyne, butyne-1, and pentyne-1 were converted into the corresponding 1-chloroalkynes at approximately the same rate when stirred for 80 hr. with 10% sodium hypochlorite. While slow, the reaction is satisfactory, particularly for the preparation of 1-chloro-1-pentyne.

Theoretically, this reaction may proceed by a carbanion, a carbonium ion, or even a free radical mechanism. Of these alternatives, we believe the carbonium ion mechanism shown below is the most probable.



Electrophilic attack of the positive chlorine ion on the resonance hybrid (IV) gives the carbonium ion (V) which is converted into the 1-chloroalkyne by loss of a proton. A free radical mechanism appears to us ruled out by the failure to isolate any product other than the chloroalkyne. A carbanion mechanism, though improbable, cannot be excluded on the basis of the present experiments. In this connection, it is proposed to investigate the behavior of other 1-alkynes with sodium hypochlorite at some future date, as syntheses of suitable alkynes will first have to be devised.

Although dehydrohalogenation has been widely used in the preparation of acetylenic hydrocarbons (6), there are few references to its application to the synthesis of chloroalkynes (2, 5). 1-Bromo-1-propyne was prepared in 25% yield (12) by dehydrohalogenation of 1,1,2-tribromopropane. No doubt, one of the reasons this method has not been exploited in the past has been the inaccessibility of the required 1,2-dichloro-1-alkenes,  $\text{RCCl}=\text{CHCl}$ . In

a previous paper of this series (9), the preparation of *cis*- and *trans*-1,2-dichloro-1-propene and their deuterated analogues was described. It was felt that these compounds might serve as starting materials for the synthesis of 1-chloro-1-propyne, depending upon the manner in which hydrogen chloride is split off by alcoholic alkali.

When *cis*-1,2-dichloro-1-propene was added to a boiling solution of potassium hydroxide in butanol, a liquid (b.p. approx. 32°C.) distilled over which was

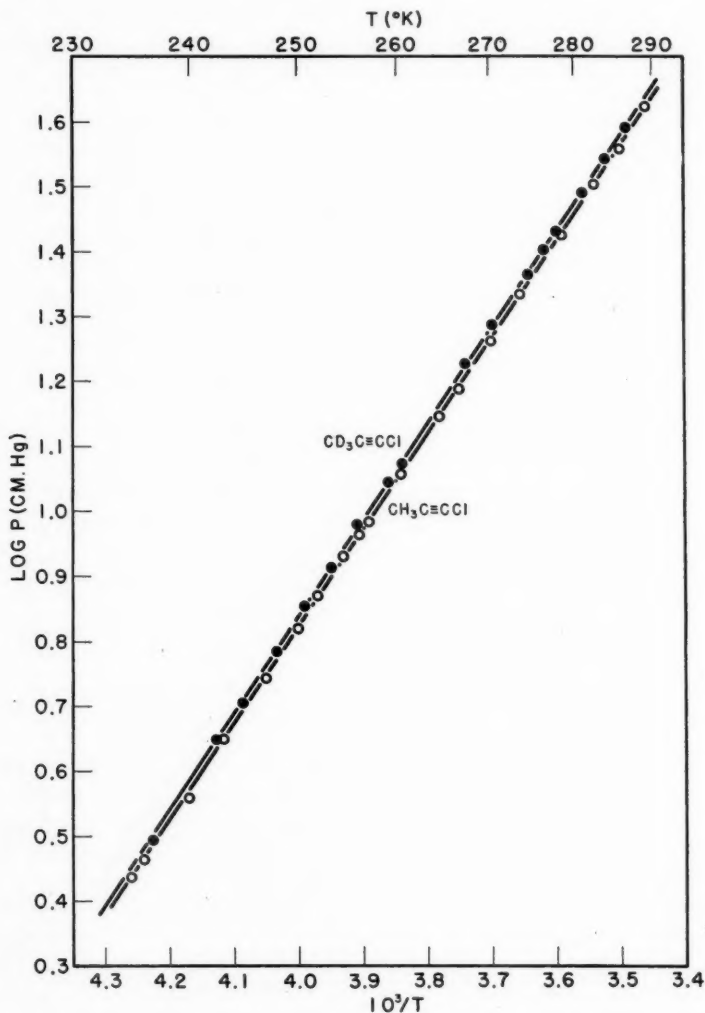


FIG. 1. Vapor pressure of 1-chloro-1-propyne and of 1-chloro-1-propyne- $d_3$ .

identified by its mass spectrum as 1-chloro-1-propyne. The alternative product, 1-chloropropadiene ( $\text{CH}=\text{C}=\text{CHCl}$ ), was recently reported by Jacobs and Brill (7) and boils at  $44^\circ\text{C}$ . The product, b.p.  $32^\circ\text{C}$ ., was identical with that obtained by chlorination of propyne with sodium hypochlorite. By treating *cis*-1,2-dichloro-1-propene- $d_4$  in the same manner, the corresponding deuterated chloropropyne was obtained.

The vapor pressures of 1-chloro-1-propyne and its deuterated analogue were measured by the method described in earlier papers of this series (9, 10, 11). The values obtained at various temperatures were then plotted logarithmically to give the curves shown on Fig. 1. For temperatures below  $16^\circ\text{C}$ ., the results were expressed by the equations

$$\log_{10} p \text{ (mm.)} = -(1.480 \times 10^3)/T + 7.740$$

and

$$\log_{10} p \text{ (mm.)} = -(1.487 \times 10^3)/T + 7.782$$

for  $\text{CH}_3\text{C}\equiv\text{CCl}$  and  $\text{CD}_3\text{C}\equiv\text{CCl}$  respectively.

The structure of 1-chloro-1-propyne was proved by chlorination at  $0^\circ\text{C}$ . to 1,1,1,2,2-pentachloropropane identical with the product recently reported by Nesmayanow, Friedlina, and Firstov (14). Furthermore, dehalogenation of the pentachloropropane with zinc dust gave 1,1,2-trichloro-1-propene.

*trans*-1,2-Dichloro-1-propene reacted much more sluggishly than the *cis*-isomer and was largely recovered after refluxing for a long period. This observation is in agreement with those of other workers who have investigated the dehydrohalogenation of 1,2-dichloroethylene (2) and of 1-ethoxy-1-chloro-1-propene (5). In each case, the *cis* form showed a considerably greater rate of reaction due also to *trans* elimination.

Dehydrohalogenation of *cis*-1,2-dichloro-1-butene and of *cis*-1,2-dichloro-1-pentene likewise gave 1-chloro-1-butyne and 1-chloro-1-pentyne respectively. These products were also identical with those obtained from the chlorination of 1-butyne and 1-pentyne by sodium hypochlorite.

The synthesis of these new chloro alkynes now completes the series to  $\text{C}_9$ .

## EXPERIMENTAL

### 1-Chloro-1-propyne

*cis*-1,2-Dichloro-1-propene (36.0 gm.) prepared as in (9) was dissolved in 20 ml. of *n*-butanol and added dropwise to a refluxing solution of 25 gm. of potassium hydroxide in 300 ml. of *n*-butanol during stirring with a magnetic bar. Water entering the reflux condenser was precooled to  $5^\circ\text{C}$ . by circulation through a copper spiral immersed in ice water in a Dewar flask. By this means loss of the volatile 1-chloro-1-propyne was avoided. After addition of the halide, the reaction mixture was cooled to  $0^\circ\text{C}$ . and the reflux condenser was replaced by a 12 in. Stedman column and a still-head. The 1-chloro-1-propyne distilled as an azeotrope, b.p.  $31$  to  $32^\circ\text{C}$ . It was dried by distillation through a U-tube containing phosphorus pentoxide on a vacuum line. Redistillation through the Stedman column gave a product, b.p.  $32.8$  to  $33^\circ\text{C}$ .,  $n_D^{20}$  1.4131 in 68% yield. The mass spectrum showed two strong peaks at 74 and 76.

### 1-Chloro-1-propyne- $d_3$

This compound was prepared from 36.4 gm. of *cis*-1,2-dichloro-1-propene- $d_4$  in exactly the same manner. The yield was 19.4 gm. (78.5%) of product b.p.  $31.7^\circ\text{C}$ . at 750 mm.,  $n_D^{20}$  1.4105. Mass spectrometric analysis: 98.17 atom % D.

### 1-Chloro-1-butyne

(a) *Dehydrochlorination method*.—*cis*-1,2-Dichloro-1-butene (20 gm.) (preparation to be described in a forthcoming paper) gave 13.2 gm. (93.5%) of 1-chloro-1-butyne, b.p.  $63\text{--}64.5^\circ\text{C}$ .,  $n_D^{20}$  1.4221. The mass spectrum showed two strong peaks at 88 and 90 corresponding to the two chlorine isotopes.

(b) *Hypochlorite method*.—A solution of sodium hypochlorite prepared on one tenth the scale reported by Smith and McLeod (16) was attached to a vacuum line which was then evacuated. 1-Butyne was introduced from a gasholder into the apparatus. After four days' stirring, all the butyne had been absorbed and there was a layer of oily liquid above the hypochlorite solution. This upper layer was separated, dried over phosphorus pentoxide on the vacuum line, and fractionated. Four liters of unreacted 1-butyne were recovered. The 1-chloro-1-butyne had b.p.  $63.5\text{--}64.5^\circ\text{C}$ .,  $n_D^{20}$  1.4210. Yield: 76%.

### 1-Chloro-1-pentyne

(a) *Dehydrochlorination method*.—*cis*-1,2-Dichloro-1-pentene (8.5 gm.) which was prepared by a method to be reported in a forthcoming paper was treated as described for the lower homologues. It gave 6.0 gm. (96%) of 1-chloro-1-pentyne, b.p.  $91.5\text{--}92.0^\circ\text{C}$ .,  $n_D^{20}$  1.4302. Calc. for  $\text{C}_5\text{H}_7\text{Cl}$ : Cl, 34.56%. Found: Cl, 33.58%.

(b) *Hypochlorite method*.—A mixture of 34.0 gm. of pentyne-1 and 800 ml. of sodium hypochlorite was stirred with a magnetic bar for 180 hr. The upper layer was then separated, dried, and fractionated. It gave 29.2 gm. (76.5%) of 1-chloro-1-pentyne, b.p.  $91.5\text{--}92.0^\circ\text{C}$ .,  $n_D^{20}$  1.4302.

### 1,1,1,2,2-Pentachloropropane

A solution of 14.0 gm. of 1-chloro-1-propyne in 50 ml. of methylene chloride was placed in a 100 ml. flask equipped with a cold finger condenser cooled with dry ice. Chlorine was introduced through a side-arm while the reaction mixture was kept at  $0^\circ$  in the dark. Five liters of chlorine were introduced in three hours. The mixture was allowed to stand at room temperature overnight, the volatile material was then removed under vacuum, and a white residue remained. Sublimation on a vacuum line gave 34.8 gm. (85% yield) of white solid, which after recrystallization from 15 ml. of petroleum ether gave 25.0 gm. of product m.p.  $179\text{--}180^\circ\text{C}$ ., identical with the value reported in (14) for 1,1,1,2,2-pentachloropropane. Dehalogenation with zinc dust in ethanol gave a liquid b.p.  $114\text{--}5^\circ\text{C}$ .,  $n_D^{20}$  1.4827, identical with the values reported for 1,1,2-trichloro-2-propene obtained by the dehydrohalogenation of 1,1,2,2-tetrachloropropane (9).

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## SOME OBSERVATIONS ON DETERMINING DENSITY OF FLUIDS BY THE FALLING DROP METHOD<sup>1</sup>

By R. P. A. SIMS

### ABSTRACT

The shape of the calibration curve obtained with a commercial Falling Drop apparatus has been investigated for drops varying in viscosity and surface tension and in media of varying solvent power. Drop velocity affects drop shape when the viscosity of the drop substance is low, and drop volume when the medium exerts solvent action on the drop. "End effect" appears to be significant even when "wall effect" is large.

### INTRODUCTION

The falling drop method has been used frequently to determine the density of fluids (3, 6, 8, 13). With most materials, nonlinear calibration curves were obtained. In a previous study (13), the parabolic calibration curve for methyl esters falling through aqueous ethanol was found to be steeper than that for glycerides and appeared to cross the curve for glycerides at high drop velocities. Drops of glycerides fell at constant rates through different portions of the tube. In contrast, the rate of fall of drops of methyl esters was observed to decrease with depth. This effect was reduced by saturating the medium with drop substance and increased by using acetonitrile instead of ethanol in the medium. Possible causes of these effects are being reported here. Although some of the characteristics are peculiar to the systems studied, others are of general interest.

The application of Stokes' law to solid and liquid spheres falling through a finite medium and factors affecting their rates of fall have been well summarized by Merrington (11). Two factors which have not been considered previously and which may also affect rate of fall are the shape of the drop and the solvent power of the medium. The shape of a drop is a function of its viscosity, surface tension, and velocity. At high rates of fall, the drop would be expected to assume a prolate spheroid shape and at low rates of fall, or at rest, to become oblate, the surface tension and viscosity of the drop substance opposing the changes in shape. In addition, when the medium exerts solvent action on the drop, diffusion into and out of the drop occurs.

### PROCEDURE

A commercial "Falling Drop Apparatus" (Fisher Scientific Co.) was used in the investigation. The media in the tubes were kept at  $25 \pm 0.003^\circ \text{C}$ . by pumping distilled water through the jacket from a constant temperature bath. Auxiliary sighting marks were inscribed on the tubes, 5 cm. above and below the regular marks, to permit measurement of rate of fall over a variety of distances.

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Contribution from the Division of Applied Biology, National Research Laboratories, Ottawa. Issued as N.R.C. No. 3250.

The materials used in this study were samples of linseed oil that had been thermally polymerized to various extents and methyl esters of  $C_{18}$  fatty acids. The media were aqueous solutions of either acetonitrile or ethanol, selected to produce desired rates of fall. Details of the technique have been published elsewhere (13).

Photographs of falling drops of triglyceride oils and methyl esters were taken through plane glass surfaces set parallel to the camera lens and film. To permit comparison of a drop at the beginning and end of its fall, both images were recorded on the same negative. Shape and area of the images were measured on 12-fold enlargements and the volumes of the corresponding solids of revolution were calculated from the axes of each drop.

Interfacial tensions were measured at  $25 \pm 0.5^\circ \text{C}$ . using a Cenco-du Nuoy tensiometer.

## EXPERIMENTAL AND RESULTS

### *Behavior of the Drop*

Deceleration of a drop during its fall could be caused by one or all of the following factors: reduction in radius due to diffusion of drop substance into the medium, decrease in density difference caused by diffusion of fat solvent from the medium into the drop, change in shape of the drop. Since falling drops of methyl ester decelerated even when the medium was saturated with drop substance and the difference in rate of fall in the saturated and unsaturated medium was insufficient to change the shape, it can be inferred that diffusion into and out of a drop takes place.

The effect of drop velocity on the shape of the drop was investigated for glycerides and esters using drops of constant size falling through media of different densities. Photographs of drops falling at slow and fast rates taken at the start and end of the timing zones were compared. They showed that drops of glycerides were spherical on release and retained their shape at velocities as high as 3 cm. per sec. Drops of ester were oblate on release but approached spherical shape on gaining speed, and at velocities greater than 1 cm. per sec. were spherical. However, even a velocity of 1.5 cm. per sec. did not cause a drop of ester to become prolate. Representative photographs of drops are shown in Fig. 1.

Volumes were calculated from the axes of the drops with an accuracy of  $\pm 1\%$  in each case. A glyceride drop, falling at 0.6 cm. per sec., did not change in volume. However, when the velocity was 3.0 cm. per sec., its volume increased by 7%. With esters falling through unsaturated media, the volume increased 4% at a speed of 0.6 cm. per sec. and 9% at 1.5 cm. per sec. When the medium was saturated with ester, the drop fell at a rate of 0.95 cm. per sec. and increased in volume by 19%.

### *Investigation of End Effect*

To determine whether adequate allowance for "end" effect had been made, rate of fall was determined using the additional sighting marks. The data (Table I), for triolein falling through aqueous ethanol, show that the lower



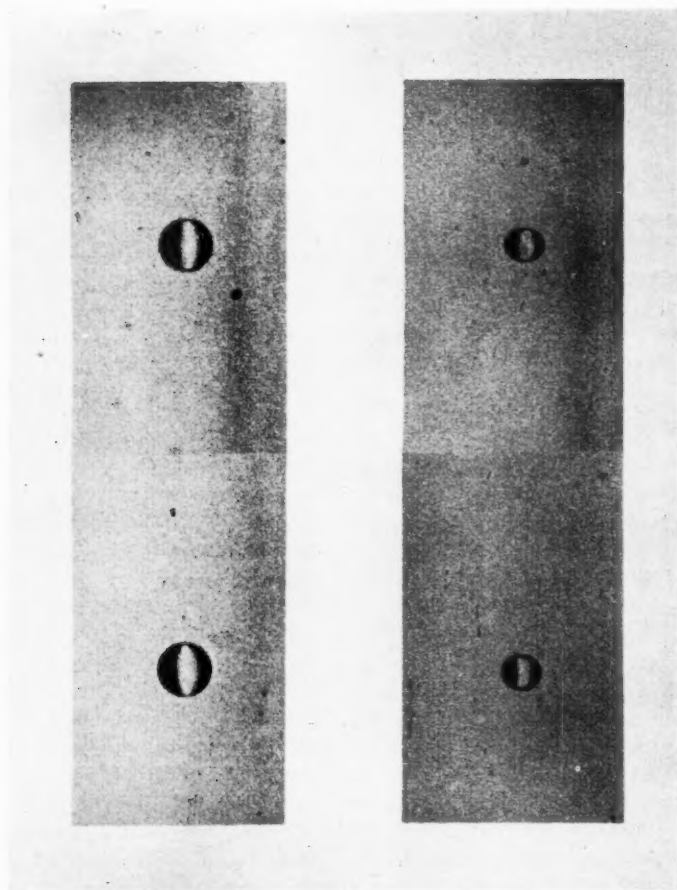


FIG. 1. Photographs of drops falling at a velocity of 0.66 cm. per sec.  
*a.* Triolein, drop volume 0.01 cm<sup>3</sup>.  
*b.* Methyl erucate, drop volume 0.005 cm<sup>3</sup>.

TABLE 1  
 EFFECT OF END ZONE ON FALLING TIME

Length of end zone, cm.		Interval, cm.	Time, sec.	Rate, cm./sec.
Top	Bottom			
12*	7*	30	45.7	0.656
7	12	30	45.6	0.658
7	7	35	53.5	0.654
7	2	40	61.4	0.651
12	2	35	53.5	0.654
17	2	30	45.7	0.656
17	12	20	30.2	0.662

\* Original end zones.

the starting point and the higher the finish line, i.e. the longer the end zones, the faster the measured rate of fall. A statistical analysis of the data, not included here, has shown that these differences are significant.

Attempts to circumvent "wall" and "end effects" by use of wider tubes failed. Under these conditions, the drops fell in an irregular manner, presumably because of convection currents.

#### *Interfacial Tension*

The interfacial tension between linseed oil and 61% ethanol was 5.9 and 6.9 dynes per cm. respectively for unheated oil and oil heated 20 hr. at 280° C. The tension between surfaces of methyl erucate and 77% ethanol was 2.1 dynes per cm.

#### DISCUSSION

When falling time was plotted as an arithmetic function of density difference between drops and media, parabolic curves were obtained:  $y = 3 + 0.47x + 0.0015x^2$  for glycerides and  $y = -2 + 0.5x + 0.0064x^2$  for esters (13). Although the curve for esters was of the same form, it crossed the glyceride plot at high drop velocities.

The parabolic form of the arithmetic plot suggests that the velocities used were too great. Since the velocities correspond to Reynolds numbers ranging from 22 down to 3, with 9 an average value, the flow of medium was generally not streamlined. Although turbulence should be avoided, slower rates of fall could not be used with the apparatus employed because of larger coefficient of variation in longer falling times. However, when the time of fall of various drops was calculated in three ways using Allen's (1) generalized equation for the motion of a sphere in a viscous medium, and the Wadell equation (14) and Newton's equation for the intermediate region of the flow, the results showed that introduction of a squared velocity term still left anomalies. The shape of the plots can therefore be attributed to a combination of excessive velocity and the following constant errors associated with the falling drop method: tangential velocity within the drop, nonspherical shape, "wall" and "end" effects, and the influence of the medium on the drop.

#### *Internal Tangential Velocity*

The viscosity of the drop substance in combination with the surface tension determines the magnitude of the internal tangential velocity and the shape of the drop. The ratio of the viscosity of glycerides and C<sub>18</sub> esters to that of the media is 25 and 5 respectively and the value of the respective interfacial tensions 6.5 and 2.1. Therefore, according to Bond (4), a drop of glyceride behaves as if it were solid. Esters, however, having approximately one-tenth the viscosity of glycerides, could have their drop velocity accelerated by a factor of 1.1. However, as Bond later pointed out (5), the interfacial tension between drop and medium may be sufficient to reduce this acceleration. If the radius of the drop is smaller than a critical radius, the drop behaves as a solid even though its viscosity is less than that of the medium. As the critical radius for methyl erucate was three times the actual radius, a drop of ester

should not be accelerated. However, the drops were travelling rapidly, causing increased tangential velocity and the critical radius may well have been less than the calculated value. Such was the case when Miyagi's (12) value for the critical radius of air in water was compared with the value calculated using Bond's expression. This effect might therefore partially account for the ester line apparently crossing the glyceride plot.

#### *Drop Shape*

Photographs showed that drops of glycerides were round at all velocities studied and that drops of ester (lower viscosity and surface tension) did not assume spherical shape until they fell at velocities greater than 1 cm. per sec. This change in shape could account for the upward bend of the ester curve at low velocities and the apparent crossing of the glyceride plot.

#### *"Wall and End Effect"*

The magnitude of the "wall" and "end effects" was estimated by calculating the velocities of a drop of linseed oil and methyl erucate using Stokes' law, Ladenburg's (9, 10) modification of it, and Bacon's (2) adaptation of Faxen's (7) correction. The following results were obtained.

Drop substance	Drop velocity, cm. per sec.			
	Stokes	Ladenburg	Faxen	Measured
Linseed oil	1.96	1.05	0.69	0.64
Methyl erucate	2.34	1.38	1.05	0.67

These results indicate that "wall" and "end effects" are significant and that, with triglycerides, the Faxen correction is applicable even at high drop velocities. When the ratio of drop radius to tube radius is larger than 0.3, the Faxen correction becomes too great. Since the measured rate of fall was slower than the most severely corrected value, it might be inferred that "end effect" is operative. The data in Table I also suggest, in contradiction of Merrington's statement, that "end effect" is appreciable when "wall effect" is large. They support Ladenburg's observation (10) that "end effect" is appreciable even if only the middle 50% of the tube is used as the timing zone.

The influence of "wall" and "end effect" on the velocity of drops of ester is about 7% less than on the larger glyceride drops. Hence, the ester falls faster than would be anticipated from consideration of drop radius alone. The diminished "wall" and "end effect" may be an additional reason for the apparent intersection of the ester and glyceride curves.

#### *Diffusion*

Another constant error was observed when methyl esters were used. Since esters are completely miscible with ethanol and acetonitrile, they might dissolve in the medium or the medium might diffuse into them. Because the rate of fall of methyl oleate through oleate-saturated 77% ethanol solution

still showed deceleration, the medium can be presumed to diffuse into the drop. Moreover, the increase in volume of the drop, calculated from photographs, was three times greater than when it fell through unsaturated medium. The more rapid deceleration in aqueous acetonitrile, in which esters are less soluble than in alcohol (13), can be explained by the larger diffusion coefficient and lower specific gravity of acetonitrile. The failure of the Faxen correction with methyl erucate can therefore be attributed to deceleration caused by solvent influence.

With a commercial Falling Drop apparatus high drop velocities must be used. When the medium exerts solvent action on the drop, the resultant turbulent flow of medium affects the drop volume by increasing the mass transfer rate. Drop velocity also governs the shape of the drop if the viscosity of the drop substance is sufficiently low. Excessive rate of fall is also directly responsible for part of the nonlinearity of the calibration curve. "Wall and end effect" are appreciable with apparatus of this type. However, the Faxen correction for "wall effect" appears to be applicable at high drop velocities. "End effect" seems to be a factor even when "wall effect" is large.

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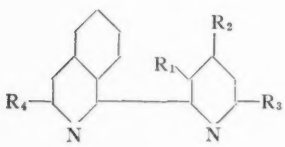
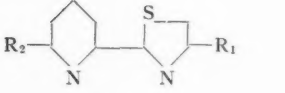
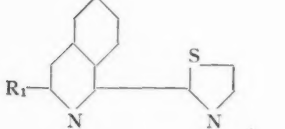
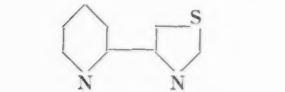
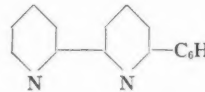
# ANALOGUES OF 2,2'-BIPYRIDYL WITH ISOQUINOLINE AND THIAZOLE RINGS. PART I<sup>1</sup>

By R. F. KNOTT AND J. G. BRECKENRIDGE

## ABSTRACT

Several analogues of 2,2'-bipyridyl, with isoquinoline, thiazole, and pyridine rings in various combinations, have been synthesized, and the effect of substituent groups in certain positions in the molecules studied with respect to their ability to react with cuprous and ferrous ion (the "cuproin" and "ferroin" reactions). The results agree with earlier work, and emphasize the desirability of two substituent groups "ortho" to the nitrogen atoms if a stable and sensitive cuprous ion reagent is wanted. The presence of one ortho substituent makes the reagent ineffective toward reaction with ferrous ion. Two of the compounds synthesized had groups in positions which did not allow a coplanar *cis* configuration of the molecule, and only in these cases were dipicrates formed; this situation is explained by assuming that hydrogen bond formation between the nitrogen atoms is not possible.

We have been engaged for some time in a study of compounds analogous to 2,2'-bipyridyl, with respect to correlations between structure and the "ferroin" and "cuproin" reactions typical of this class of compounds. The examples we have prepared are illustrated below; to conserve space they are referred to subsequently in the text by Roman numerals.

	Compound	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>
	I	H	H	H	H
	II	H	CH <sub>3</sub>	H	H
	III	CH <sub>3</sub>	H	H	H
	IV	H	H	H	CH <sub>3</sub>
	V	CH <sub>3</sub>	H	H	CH <sub>3</sub>
	VI	H	H	CH <sub>3</sub>	CH <sub>3</sub>
	VII	H	CH <sub>3</sub>	H	CH <sub>3</sub>
	VIII	H	H		
	IX	CH <sub>3</sub>	CH <sub>3</sub>		
	X	CH <sub>3</sub>	H		
	XI	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>		
	XII	C <sub>6</sub> H <sub>5</sub>	H		
	XIII	H			
	XIV	CH <sub>3</sub>			
					
					

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These were prepared by conventional methods, those containing an isoquinoline ring by reaction of the appropriate pyridyllithium or thiazolylithium with isoquinoline or 3-methylisoquinoline, and the pyridyl-thiazole compounds by ring-closure methods.

In the course of the synthetic work, the bases were characterized by preparation of picrates. It is well known that compounds such as 2,2'-bipyridyl and 1,10-phenanthroline form only monopicates, for which a possible explanation might lie in the situation discussed by Mann and Watson (8) for some other types of molecule. This involved the effect of a proton attached to one nitrogen atom on the proton-attracting power of a second nitrogen atom. Another possible explanation in the present case is that a hydrogen bond may be formed between the nitrogen atoms by the first proton, but where the two rings are free to rotate about the bond connecting them they will presumably take up the coplanar *trans* configuration; this has been shown to be so for 2,2'-bipyridyl by Cagle (1) and Fielding and LeFevre (5). In such a case the hydrogen bond would have to be sufficiently strong to hold the molecule in the *cis* configuration. In the present work, examination of molecular models has shown that in two cases (compounds III and V) steric hindrance is such that it would be extremely difficult for the two rings to take up the coplanar *cis* arrangement, and thus a hydrogen bond is improbable; in agreement with the hydrogen bond theory, we have found that these two compounds are the only ones which form dipicates. The ultraviolet absorption spectra of all the compounds were determined in ethanol solution, and in a few cases in dilute acid, in the hope that in the latter a significant difference might appear between, for example, compounds I and III. The molar extinction coefficients at the wave length of maximum absorption are given in Table I, and it is evident that there are no anomalous results.

TABLE I  
ULTRAVIOLET ABSORPTION SPECTRA

Compound	95% ethanol		0.05 N HCl	
	$\lambda$ (m $\mu$ )	$\epsilon_{\text{max}} \times 10^{-3}$	$\lambda$ (m $\mu$ )	$\epsilon_{\text{max}} \times 10^{-3}$
I	222	41.8	232	30.0
II	222	42.8	—	—
III	219	49.5	232	32.0
IV	223	47.5	—	—
V	222	54.2	—	—
VI	223	43.8	—	—
VII	223	46.2	—	—
VIII	(232), 301	(4.05), 13.8	—	—
IX	(233), 312	(4.12), 13.8	—	—
X	(235), 309	(4.83), 13.3	—	—
XI	253, (324)	20.8, (10.3)	—	—
XII	251, (322)	25.1, (10.8)	—	—
XIII	233	28.4	234	28.0
XIV	235	29.2	—	—
XV	249, (287)	12.1, (8.52)	—	—
XVI	236	21.4	—	—

Secondary maxima in parentheses.

We have investigated the reactions of the compounds with ferrous and cuprous ion; it was evident from their structures that they could be divided into three classes: (a) those with one or two groups in positions "ortho" to the nitrogen atoms (IV, VI, VII, IX, X, XI, XII, XIV, XVI), which would be expected to give only the cuproin reaction, (b) those with no "ortho" groups (I, II, VIII, XIII, XV), which should give both ferroin and cuproin reactions, and (c) those in which steric hindrance to coplanarity of the rings is such as to preclude formation of any stable chelate product (III, V). The colorimetric work along these lines is summarized below.

The nine compounds in class (a) and two compounds (I, II) in class (b) gave highly colored complexes with cuprous ion, extractable by isoamyl alcohol; the absorption spectra in the visible region are shown in Figs. 1 and 2. It may be seen that two "ortho" groups result in a complex with a higher extinction

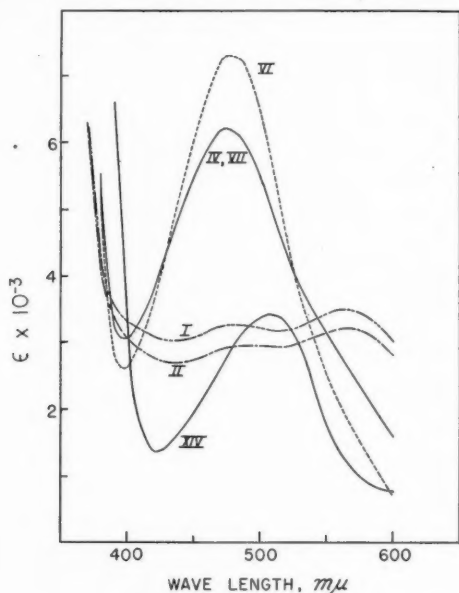


FIG. 1. Absorption spectra of copper complexes of compounds I, II, IV, VI, VII, XIV.

coefficient than if only one or no "ortho" group is present, and that a methyl group is more effective than a phenyl. It might be supposed that the ortho groups would make the complex more stable, for example toward oxidation of the cuprous ion. We hope to be able to report values for the stability constants of these complexes soon. The three class (b) compounds whose spectra are not given (VIII, XIII, XV) gave unstable cuprous complexes of low color intensity, emphasizing the point that for a stable and sensitive cuprous ion reagent of this type, the two "shielding" groups are apparently a necessity. Molecular models of these complexes show that with tetrahedral co-ordination



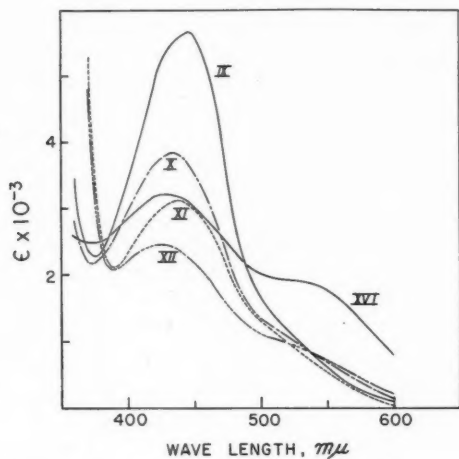


FIG. 2. Absorption spectra of copper complexes of compounds IX, X, XI, XII, XVI.

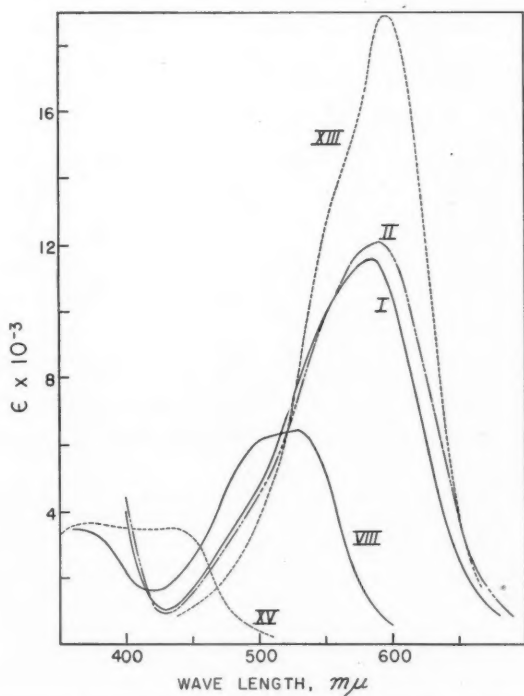


FIG. 3. Absorption spectra of iron complexes of compounds I, II, VIII, XIII, XV.

of the two organic molecules around the cuprous ion, the latter is almost completely shielded from view. It may also be seen that replacement of a pyridine ring by thiazole results in a lowering of the extinction coefficient; compare XII and XVI, and IV and XIV.

The five compounds in class (b), as expected, gave colored complexes with ferrous ion, the absorption spectra for which are given in Fig. 3. With these complexes, replacement of pyridine by thiazole leads to a marked increase in extinction coefficient (compare I and XIII). Previous work by Erlenmeyer (4) had shown that 2,2'- and 4,4'-bithiazoles gave no stable colored complexes with ferrous ion, and the result obtained in this work was somewhat unexpected.

The two compounds in class (c) gave no color with ferrous ion, and with cuprous ion gave unstable yellow colors of low intensity.

For convenience in comparing the extinction coefficients at the wave lengths of maximum absorption, these are given in Table II.

TABLE II  
SPECTRAL DATA FOR IRON AND COPPER COMPLEXES

Compound	Iron complex		Copper complex	
	$\lambda$ (m $\mu$ )	$\epsilon_{\max}$	$\lambda$ (m $\mu$ )	$\epsilon_{\max}$
I	585	11,600	560	3,500
II	590	12,100	565	3,200
III	—	—	—	—
IV	—	—	475	6,200
V	—	—	—	—
VI	—	—	480	7,300
VII	—	—	475	6,200
VIII	525	6,500	—	—
IX	—	—	445	5,700
X	—	—	435	3,800
XI	—	—	440	3,100
XII	—	—	425	2,500
XIII	600	18,900	—	—
XIV	—	—	510	3,400
XV	370,440	3,600	—	—
XVI	—	—	425	3,200

The ferroin reaction with the five class (b) compounds was investigated more fully, and values for their over-all stability constants calculated. Beer's Law was shown to hold for I, II, and XIII, and the method of continuous variations was used to confirm the probability that in the final complex there are three molecules of the reagent per ferrous ion. This was found to be the case with I and XV, and was assumed to be true for the others. To a solution containing known amount of ferrous ion were added increasing quantities of the reagent, and a curve was plotted relating absorbance and moles reagent per mole ferrous ion. This was done for I, II, XIII, and XV; in each case  $K$  was calculated from at least three points on the curve, and concordant results were obtained. These of course neglect any light absorption due to the ferrous ion, which at the concentrations used was very small. For compounds I, II,

and XV the solvent was 10% aqueous ethanol, buffered to pH 5.1, and for compound XIII the solvent was 60% acetic acid; the temperature was 28° C. The following values for log *K* were obtained: I, 9.36; II, 9.94; XIII, 8.50; XV, 11.53.

Further work is in progress on the synthesis and examination of other compounds of similar type.

#### EXPERIMENTAL

All melting points are corrected: microanalyses by Micro-Tech Laboratories, Skokie, Ill. (Table III). A Beckmann Model DU spectrophotometer was used for the colorimetric work.

##### *Compounds I, II, III, IV, V, VI, VII, XIII, XIV*

The procedure for all these was essentially that developed by Gilman and co-workers (6); detailed directions are given below only for compound I.

To a solution of 9.1 gm. (0.0577 mole) of 2-bromopyridine in 25 ml. ether at -40° C. was added an equimolar amount of *n*-butyllithium solution. The mixture was stirred gently for 15 min., and then 12.9 gm. (0.1 mole) of isoquinoline in 25 ml. ether was added slowly. The mixture was kept at -35° C. to -20° C. for four hours, with stirring. Slightly less than the equivalent amount of dilute hydrochloric acid was added to effect hydrolysis, and the alkaline aqueous phase extracted with ether. After removing the ether, the red, oily residue was heated with 15 ml. of nitrobenzene at 130° C. for one hour, after which the nitrobenzene was distilled off *in vacuo* (15 mm.). The residue distilled at 135-145° C. at 0.2 mm. pressure, giving a yellow oil which was purified by decolorization and recrystallization from ligroine-ether, yielding 2.44 gm. (20.7%) of white crystals of 1-(2-pyridyl)isoquinoline.

In four cases (II, III, VI, XIII) the crude product could not be crystallized. With two of these (II, XIII) crystals were eventually obtained after conversion to the picrate, purification, and liberation of the free base. With the remaining two (III, VI) even this procedure failed to yield crystals, and the final product was obtained as an oil after redistillation under high vacuum.

##### *Compound XVI*

To a solution of phenyllithium prepared from 6.7 gm. (0.043 mole) of bromobenzene and 0.625 gm. (0.09 mole) lithium in 50 ml. ether was added 5 gm. (0.032 mole) of 2,2'-bipyridyl in 50 ml. ether. The dark red solution was stirred and refluxed gently for three hours, and allowed to stand overnight at room temperature. The mixture was hydrolyzed by cold dilute hydrochloric acid, and the ether layer further extracted with acid. The acid extracts were made alkaline and extracted with ether. After removing the ether, oxidation by nitrobenzene and vacuum distillation produced an oil, b.p. 145-155° C. at 0.2 mm. Crystallization from ligroine-ether gave 0.68 gm. (8.9%) of white crystals of 6-phenyl-2,2'-bipyridyl.

##### *2-Cyanopyridine, 2-Cyano-6-methylpyridine*

The procedure used by Craig (3) for the preparation of the former was extended to the 6-methyl derivative, which was obtained as white needles,

m.p. 72–72.5° C., in 40% yield. Calc. for  $C_7H_6N_2$ : N, 23.73%. Found: N, 23.93, 23.86%.

*Pyridine-2-thiocarboxamide, 6-Methylpyridine-2-thiocarboxamide*

The procedure used by Karrer (7) for the preparation of the former was used in both cases. The 6-methyl derivative was obtained in 70% yield as yellow-green plates, m.p. 103–104° C.

*Compounds IX, X*

Chloroacetone was condensed with the two thiocarboxamides noted above, following the procedure of Karrer (7) for compound X.

TABLE III

Compound	Compounds I–XVI				Picrates		
	Yield	M.p., ° C.	Analyses		M.p., ° C.	Analyses	
			Calc., %	Found, %		Calc., %	Found, %
I	20.7%	74.5–75.3	C, 81.51 H, 4.88 N, 13.62	81.42, 81.45 5.01, 5.03 13.46, 13.60	167.2–168	N, 16.10	16.15, 16.10
II	14.8%	55.2–55.8	C, 81.80 H, 5.49 N, 12.72	81.79, 81.86 5.53, 5.39 12.60, 12.70	161–161.5	N, 15.61	15.55, 15.42
III	29.2%	b.p. 165° C. at 0.35 mm.	C, 81.80 H, 5.49 N, 12.72	81.70, 81.60 5.72, 5.50 12.60, 12.56	156–156.5	*C, 47.80 H, 2.66 N, 16.52	48.01, 47.70 2.62, 2.49 16.54, 16.61
IV	24.4%	75.6–76.3	C, 81.80 H, 5.49 N, 12.72	81.72, 81.65 5.59, 5.40 12.64, 12.44	177–177.6	N, 15.61	15.87, 16.15
V	16.0%	71.5–72	C, 82.01 H, 6.02 N, 11.96	82.13, 82.26 6.13, 6.18 11.76, 11.81	170–170.5	C, 57.00 H, 3.70 N, 15.11	57.55, 57.43 3.51, 3.51 15.33, 15.20
					140–141	*C, 48.56 H, 2.91 N, 16.19	49.03, 49.20 2.83, 2.89 16.27, 16.01
VI	16.5%	b.p. 142° C. at 0.15 mm.	C, 82.01 H, 6.02 N, 11.96	82.03, 81.82 6.25, 5.96 11.86, 11.82	170–171	N, 15.11	15.20, 15.24
VII	16.0%	75–75.6	C, 82.01 H, 6.02 N, 11.96	81.96, 81.79 6.19, 6.11 11.95, 12.10	162–162.5	N, 15.11	15.57, 15.32
VIII	1%	46–46.3	—	—	—	—	—
IX	73.5%	93–93.3	C, 63.11 H, 5.30 N, 14.73	63.04, 63.07 5.24, 5.41 14.28, 14.50	191.5–192	N, 16.70	16.20, 16.43
X	72%	84–84.5	—	—	—	—	—
XI	82%	127–127.5	C, 71.40 H, 4.80 N, 11.11	71.90, 71.76 4.80, 4.86 11.00, 11.10	203–203.5	N, 14.55	14.62, 14.41

\* Calculated values for dipicrate, all others for monopicrate.

TABLE III (Concluded)

Compound	Compound I-XVI				Picrates		
	Yield	M.p., ° C.	Analyses		M.p., ° C.	Analyses	
			Calc., %	Found, %		Calc., %	Found, %
XII	77%	72.5-73	C, 70.54 H, 4.23 N, 11.77	70.74, 70.79 4.32, 4.21 11.52, 11.40	141-142	N, 14.98	14.51, 14.76
XIII	7.8%	73.4-73.7	C, 67.89 H, 3.80 N, 13.20	68.28, 68.26 3.74, 3.90 13.28, 13.15	140-141.3	N, 15.87	15.84, 15.75
XIV	4.2%	68.8-69.2	C, 68.99 H, 4.45 N, 12.38	69.59, 69.68 4.69, 4.56 12.34, 12.40	136-136.5	N, 15.74	15.43, 15.45
XV	18.5%	103-103.5	C, 59.25 H, 3.72 N, 17.28	59.52, 59.65 3.85, 3.93 17.26, 17.47	—	—	—
XVI	8.9%	83.5-84.5	C, 82.72 H, 5.21 N, 12.06	83.02, 82.89 5.23, 5.34 11.66, 11.85	173.8-174	N, 15.22	15.20, 15.20

*Compounds XI, XII*

A condensation similar to the above, but substituting  $\omega$ -chloroacetophenone for chloroacetone, was used. Since the procedures were identical, only that for XII is given.

To a solution of 1.5 gm. (0.0108 mole) of pyridine-2-thiocarboxamide in 10 ml. absolute ethanol was added 1.7 gm. (0.0110 mole) of  $\omega$ -chloroacetophenone; the mixture was refluxed for two hours, and after it had been allowed to stand overnight at room temperature, was refluxed for two more hours. The solution was evaporated to half its volume and cooled; the precipitate which appeared was filtered and washed with dilute potassium hydroxide solution, and then crystallized from ligroine-ether. The white cubic crystals of 2-(2-pyridyl)-4-phenylthiazole weighed 1.99 gm. (77%).

*Compound VIII*

Pyridine-2-thiocarboxamide (5.1 gm., 0.037 mole) and ethyl  $\alpha,\beta$ -dichloroethyl ether (5 gm., 0.043 mole) were dissolved in 40 ml. 75% ethanol. The solution was refluxed for two hours, concentrated to half its volume, and allowed to stand overnight. The tarry mixture was made alkaline with sodium carbonate, and steam-distilled until the distillate no longer gave a red color with ferrous sulphate; about 400 ml. of distillate was obtained. Ether extraction of the distillate resulted in a small quantity of yellow oil, which darkened slowly on standing, but finally crystallized. Sublimation gave 0.032 gm. (1%) of white crystals of 2-(2-pyridyl)-thiazole. Analyses were not done, but the very great similarity of the ultraviolet absorption spectrum of the product to those of the closely related compounds IX and X left no doubt as to its structure.

### Compound XV

A sample of 2-( $\omega$ -bromo)acetylpyridine (3.5 gm., 0.0175 mole) was prepared from 2-acetylpyridine by the method of Clemo (2). To this, dissolved in 50 ml. absolute ethanol, was added 1.2 gm. (0.02 mole) of thioformamide in 10 ml. absolute ethanol. A vigorous reaction ensued and the mixture became dark green; it was refluxed gently for four hours, made alkaline with potassium carbonate, and steam-distilled. About 500 ml. of distillate was obtained, which deposited a few crystals on cooling. Slow evaporation produced an additional amount of crystalline material, and purification by sublimation gave 0.503 gm. (18.5%) of 4-(2-pyridyl)thiazole.

### Reactions with Cuprous Ion

Standardized aqueous solutions of copper containing 5-30 p.p.m. were prepared.

To 25 ml. of a copper solution of known strength in a separating funnel was added sufficient hydroxylamine hydrochloride to reduce cupric to cuprous ion, and the pH was then adjusted to 6 with a sodium acetate buffer. About 10 ml. of a solution of the reagent in purified isoamyl alcohol (containing about 0.1 gm. of reagent) was added, and the contents of the funnel shaken vigorously. The aqueous layer was removed and the alcohol solution transferred to a 50 ml. volumetric flask. The aqueous layer was extracted with further portions of the alcohol solution until the extract was colorless, and the total alcohol extract was made up to 50 ml. Absorbance values were measured on the alcohol solutions, readings being taken every 5  $m\mu$  except near the maxima, where the intervals were 2  $m\mu$ . Beer's Law was shown to hold for compound VI, readings being taken at 480  $m\mu$  with copper solutions of different strengths.

### Reactions with Ferrous Ion

Standardized aqueous solutions of iron were prepared containing 0.7-30 p.p.m. of ferrous ion.

#### (a) Method of Continuous Variations

Since the reagents were colorless, and any absorbance due to ferrous ion in the concentrations used was negligible, curves were plotted of absorbance (the "Y" function) against "x". "X" ml. of reagent solution (0.001036 *M*) were added to (1 - x) ml. of ferrous ion solution of the same concentration, all solutions being buffered to pH 5.1. With the two compounds tested (I, XV) sharp maxima were obtained at  $x = 0.75$ , i.e. the complexes were of the type  $FeR_3^{++}$ .

#### (b) Stability Constants

Absorbances were measured of a number of solutions containing 25 ml. of 0.0001945 *M* iron solution and varying amounts of 0.01459 *M* reagent solution, buffered to pH 5.1, and made up to 50 ml. at 28° C. Readings were made at 585  $m\mu$ , and the results plotted. Calculation of the constant  $K = [FeR_3^{++}]/([Fe^{++}][R]^3)$  was done for three points on the sloping part of the curve; the results obtained with I were:  $2.22 \times 10^9$ ,  $2.37 \times 10^9$ , and  $2.31 \times 10^9$ . The average value was  $2.30 \times 10^9$ , or  $\log K = 9.36$ .

## ACKNOWLEDGMENT

We wish to acknowledge with thanks financial support from the Advisory Committee on Scientific Research, University of Toronto, and the award of fellowships by the Research Council of Ontario and Canadian Industries Limited to one of us (R.F.K.).

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## IRRADIATION OF CHLOROFORM-WATER SYSTEMS WITH $\text{Co}^{60}$ GAMMA-RAYS AND BETATRON X RAYS<sup>1</sup>

By R. W. HUMMEL, A. B. VAN CLEAVE, AND J. W. T. SPINKS

### ABSTRACT

The production of acid from two commercial brands of chloroform, on exposure to  $\text{Co}^{60}$  gamma-rays and high energy X rays from a betatron, has been measured. Inhibitor-free chloroform liberates acid in amounts varying linearly with the radiation dose. The specific yield, in micromoles of acid produced per liter of chloroform per kiloroentgen, varies inversely as the square root of the dose rate. The specific yields are slightly less for betatron radiations, compared with  $\text{Co}^{60}$  gamma-rays. The average lifetime of the free radical chains is about one second.

### INTRODUCTION

Polyhalogenated aliphatic and aromatic compounds are radiation sensitive, decomposing chainwise to form halogen acids. The possibilities of adapting chloroform to make a satisfactory dosimeter have been extensively studied, especially concerning its use as a personnel dosimeter (5).

Commercial chloroforms of all grades contain inhibitors such as ethanol which must be removed if high sensitivity to X and gamma radiation is desired. Water and oxygen increase the sensitivity (2). The alcohol is easily removed by multiple extractions with distilled water, and the resulting product, containing water and dissolved oxygen, is highly sensitive to X and gamma radiations. The washed chloroform is, however, sensitive to visible and ultraviolet light and decomposes on heating. The rate of acid production increases with increasing temperature and decreasing dose rate, and is energy dependent in the 50–830 kev. range (5).

The purposes of the present investigation were to determine the energy dependence, if any, of chloroform to electromagnetic radiations from 1–24 Mev. and to determine the nature of the dose rate dependence.

### MATERIALS

British Drug Houses AnalaR and Mallinckrodt Analytical Reagent chloroform were used. Each was prepared for irradiation in the same way, by shaking 10 times with equal volumes of distilled water in a separatory funnel. This procedure was followed to remove alcohol, generally included by the manufacturers as a preservative. The washed chloroform was kept under a layer of distilled water, in a brown screw-capped bottle. No appreciable amounts of acid were produced during periods up to a week, nor did the radiation sensitivity change. At least 12 hr. elapsed between washing and irradiating.

The water used throughout was tap water distilled once in an all-Pyrex apparatus from an alkaline permanganate solution. Water redistilled from alkaline manganous hydroxide suspension was used once, but no difference in the results was observed. B.D.H. bromocresol purple was used as an indicator.

<sup>1</sup> Manuscript received December 21, 1953.

Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Saskatchewan.

## EXPERIMENTAL METHODS

For irradiations with  $\text{Co}^{60}$  gamma-rays, 3-ml. portions of chloroform were pipetted into glass-stoppered  $13 \times 100$  mm. Pyrex tubes, 2 ml. of distilled water were added, and the samples irradiated. The tubes were not shaken before or immediately after irradiating. After irradiation, the contents of a tube were poured into a 10-ml. Erlenmeyer flask and a glass-enclosed stirring magnet was added. The tube was rinsed twice with 1-ml. portions of distilled water, the rinse waters being added to the flask. Ten drops of bromocresol purple solution (1.5 gm. per liter, pH about 3.5) were added, and the mixture titrated with  $ca. 10^{-2} N$  sodium hydroxide solution from a microburette until the color of the indicator (just off yellow) matched that of a blank, the latter having received identical treatment except for irradiation. If the pH of the indicator solution had been any higher, the blank color would have been too far off yellow, i.e., the apparent pH would have been greater than about 5.2. It was not feasible to titrate to a purple color (pH about 7.0) since in almost every case the purple color could not be obtained by treating irradiated samples with indicator, base, etc. The nonirradiated chloroform samples could always be taken to the purple color region. It appeared that the greater the dosage received, the more difficult it was to titrate to a purple end point. However, by having the blank at about pH 5.2, it was relatively easy to obtain a color match.

For irradiation with betatron X rays, 2-ml. portions of chloroform overlaid with 2 ml. distilled water were used.

The irradiations were done at  $25 \pm 2^\circ\text{C}$ . unless otherwise stated.

To determine the average lifetime of the chains leading to acid production, a rotating sector was used. This consisted of a steel cylinder, 12 in. long and  $6\frac{1}{4}$  in. in diameter, mounted on roller bearings and rotated, via a variable-speed motor and pulley system, at speeds from about 1–4800 r.p.m. Two sectors, 3.5 cm. deep, were cut out of the cylinder, each subtending an angle

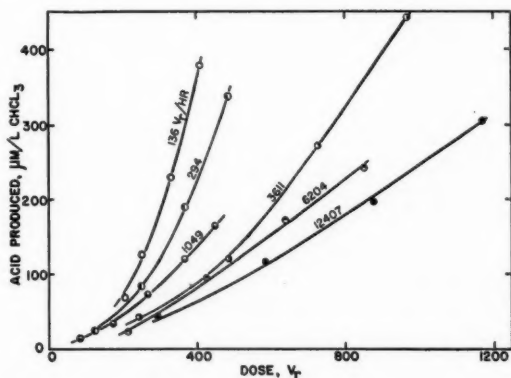


FIG. 1. Irradiation of AnalaR  $\text{CHCl}_3$  with  $\text{Co}^{60}$  and betatron radiations. Amounts of acid produced ( $Y$ ) as a function of Victoreen r.-meter readings,  $V_r$  at various dose rates,  $V_r$  per hour.

of 60° at the center (see Fig. 7). Rotation rates were determined visually at low speeds and with a tachometer or Strobotac at high speeds. The calculated ratio of the dose rates in the "dark" and "light" periods was 0.0027. The measured ratio was about 0.014. The difference is due presumably to scattered radiation from the walls of the room containing the 1000-c. source.

### RESULTS

The results of irradiations of B.D.H. AnalaR chloroform are given in Table I and plotted in Fig. 1. All results are in terms of readings obtained on a Victoreen r.-meter, corrected for temperature and pressure effects. These readings were obtained with the sensitive volume of the thimble chamber inside a glass tube placed, in turn, in a hole in a Lucite block. The details of the experimental arrangements have been given elsewhere (3).

TABLE I  
IRRADIATION OF CHLOROFORM-WATER SYSTEMS WITH Co<sup>60</sup> AND BETATRON RADIATIONS  
(B.D.H. ANALAR CHLOROFORM)

Source	Photon energy (Mev.)	Dose rate ( $V_r$ /hr.)	Dose ( $V_r$ )	Yield ( $\mu$ M. acid per liter CHCl <sub>3</sub> )
1000 c. Co <sup>60</sup>	1.25	136	205	69.3
			250	126.4
			330	229.8
			409	378.4
1.2 c. Co <sup>60</sup>	1.25	294	123	25.7
			249	84.2
			366	189.6
			485	338.0
1.2 c. Co <sup>60</sup>	1.25	1049	83	16.2
			172	35.3
			266	73.6
			366	121.3
			449	164.3
Betatron	24 Mev. peak	3611	242	43.0
			484	119.7
			726	272.0
			968	441.7
Betatron	18 Mev. peak	6204	213	24.2
			426	94.6
			639	172.0
			852	241.7
Betatron	24 Mev. peak	12407	292	44.9
			584	116.9
			876	197.3
			1068	305.4

The square root of the yield ( $Y$ ) in  $\mu$ M/l. is plotted versus the dose ( $D$ ) in Victoreen roentgens in Fig. 2. The equations of the lines, calculated by the method of least squares, are given in Table II.

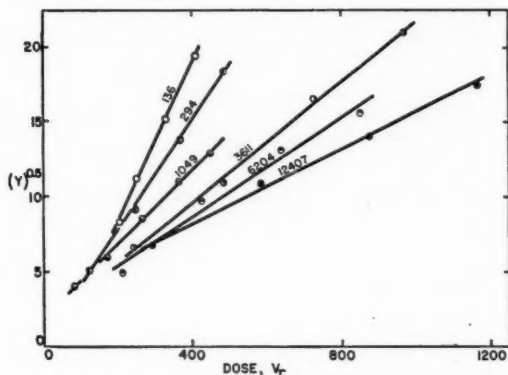


FIG. 2. Irradiation of AnalaR  $\text{CHCl}_3$  with  $\text{Co}^{60}$  and betatron radiations. Replot of the data to show the linear relationship between  $Y^{1/2}$  and the dose ( $D$ ) in Victoreen r.-meter readings.

TABLE II  
IRRADIATION OF CHLOROFORM-WATER SYSTEMS WITH  $\text{Co}^{60}$  AND BETATRON RADIATIONS—  
NONLINEAR RELATIONSHIP BETWEEN YIELD AND DOSE (B.D.H. ANALAR CHLOROFORM)

Dose rate ( $V_r$ /hr.)	Least squares line
136	$\sqrt{Y} = 0.0534D - 2.35$
294	$= 0.0368D + 0.37$
1049	$= 0.0246D + 1.92$
3611	$= 0.0202D + 1.54$
6204	$= 0.0165D + 2.04$
12407	$= 0.0122D + 3.35$

The results of irradiations of Mallinckrodt A.R. chloroform with  $\text{Co}^{60}$  and betatron radiations are given in Table III. The individual results used to obtain the least squares lines given in Table III are plotted, together with those

TABLE III  
IRRADIATION OF CHLOROFORM-WATER SYSTEMS WITH  $\text{Co}^{60}$  AND BETATRON RADIATIONS—  
LINEAR RELATIONSHIP BETWEEN YIELD AND DOSE (MALLINCKRODT A.R. CHLOROFORM)

Source	Dose rate*	Least squares line
$\text{Co}^{60}$	176 $V_r$ /hr.	$Y = 2.85 D - 65.8$
$\text{Co}^{60}$	292	$= 2.17 D - 52.8$
$\text{Co}^{60}$	1037	$= 1.25 D - 10.5$
$\text{Co}^{60}$	4056	$= 0.691D - 25.8$
Betatron (23 Mev. peak)	$638 \pm 7$	$= 1.44 D - 26$
Betatron (23 Mev. peak)	$1245 \pm 6$	$= 1.04 D$
Betatron (23 Mev. peak)	$2735 \pm 54$	$= 0.732D + 34.5$
Betatron (23 Mev. peak)	$3373 \pm 23$	$= 0.648D + 7.25$
Betatron (21 Mev. peak)	$11850 \pm 227$	$= 0.397D - 24.5$

\*The variation in dose rate during a given betatron irradiation was calculated by timing the "clicks" for short periods throughout the irradiation, a special effort being made to keep the click rate constant by manipulation of the betatron controls. The deviations given in Table III are the standard deviations. Since the dose rate varies across the betatron beam, being greatest at the center, the tubes were placed in the center holes of the rotating Lucite block.

By "click" is meant the sound heard when a monitor fixed in the X-ray beam is discharged. This occurs when the monitor has received a definite amount of radiation.

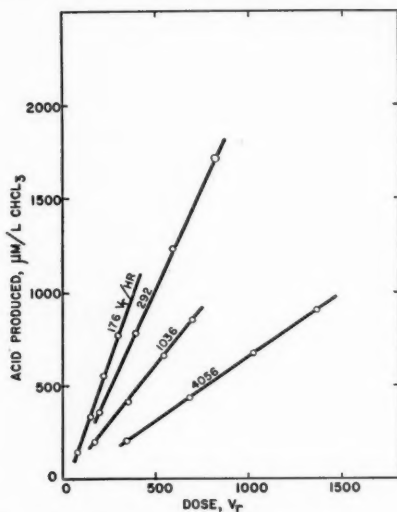


FIG. 3. Irradiation of Mallinckrodt  $\text{CHCl}_3$  with  $\text{Co}^{60}$  gamma-rays. Linear relationship between  $Y$  and  $D$  for various dose rates.

lines, in Fig. 3 ( $\text{Co}^{60}$ ) and Fig. 4 (betatron). The slopes in  $\mu\text{M./l./1000 } V_r$ , symbol  $S$ , are plotted versus the inverse square root of the dose rate in 1000  $V_r/\text{hr.}$ , symbol  $R$ , in Fig. 5. The equations of the resulting straight lines are given in Table IV.

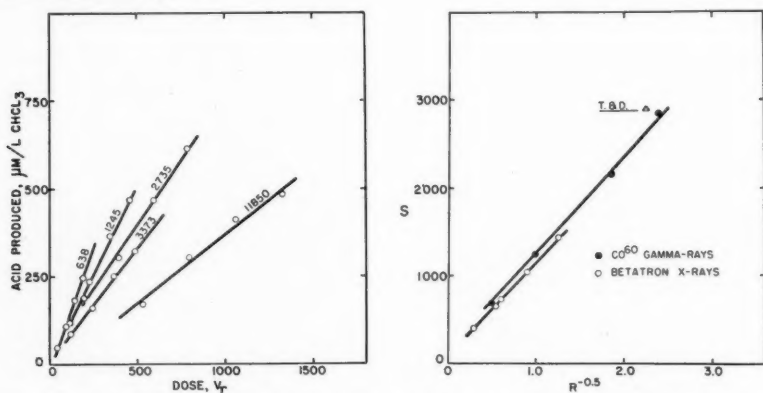


FIG. 4. Irradiation of Mallinckrodt  $\text{CHCl}_3$  with betatron X rays at various dose rates.

FIG. 5. Irradiation of Mallinckrodt  $\text{CHCl}_3$  with  $\text{Co}^{60}$  and betatron radiations. Linear relationships between specific yield ( $S$ ) and the square root of the reciprocal of the dose rate ( $R$ ).

The specific yield,  $S$ , found by Taplin *et al.* (5) with 200 r./hr. of Ra gamma-rays, is also plotted in Fig. 5.

To determine the average chain lifetime, the rotating sector was operated at rotation rates from 1–2230 r. p. m. Some samples were irradiated for half-

TABLE IV  
IRRADIATION OF MALLINCKRODT CHLOROFORM—RELATIONSHIP BETWEEN SPECIFIC YIELD AND DOSE RATE

Source	Least squares line
Co <sup>60</sup>	$S = 1098 \cdot R^{-\frac{1}{2}} + 172$
Betatron	$S = 1073 \cdot R^{-\frac{1}{2}} + 81.8$

hour periods with the sector stopped; other samples were irradiated with the sector rotating for one and one-half hour periods in order to give each sample the same total exposure to the gamma-ray beam. Actually, Victoreen readings taken under these conditions, agreed within 1.5%. The amounts of base required ( $A_i$ ) to titrate samples irradiated intermittently were greater than those required ( $A_s$ ) for samples irradiated with the steady beam. The difference is expressed as a percentage increase in Fig. 6.

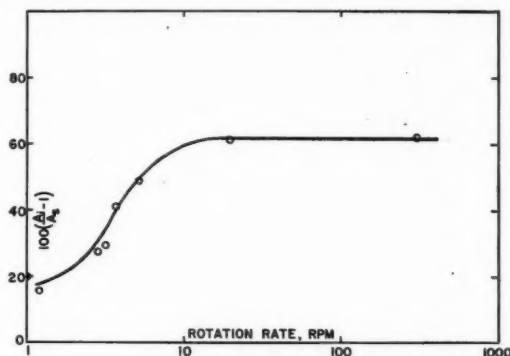


FIG. 6. Effect of intermittent irradiation of Mallinckrodt  $\text{CHCl}_3$  with  $\text{Co}^{60}$  gamma-rays.

#### DISCUSSION

The difference in the results obtained with B.D.H. AnalaR chloroform and Mallinckrodt Analytical Reagent chloroform has been traced to the presence of an unsaturated, water-insoluble compound present in the former. It is removable by shaking the AnalaR chloroform at least five times with portions of slightly basic potassium permanganate solution (ca. 0.5 gm. potassium permanganate per liter of solution), followed by one extraction with concentrated hydrochloric acid to remove manganese dioxide, and 10 extractions with distilled water. The results obtained after such treatment were almost exactly the same as were obtained with Mallinckrodt chloroform. Treatment of the latter with potassium permanganate solution did not alter its response to  $\text{Co}^{60}$  radiations. The foreign substance in the B.D.H. AnalaR chloroform has not been identified.

The mechanism of the radiation-induced reaction has been discussed by Cronheim and Gunther (2). However, their mechanism does not apply to

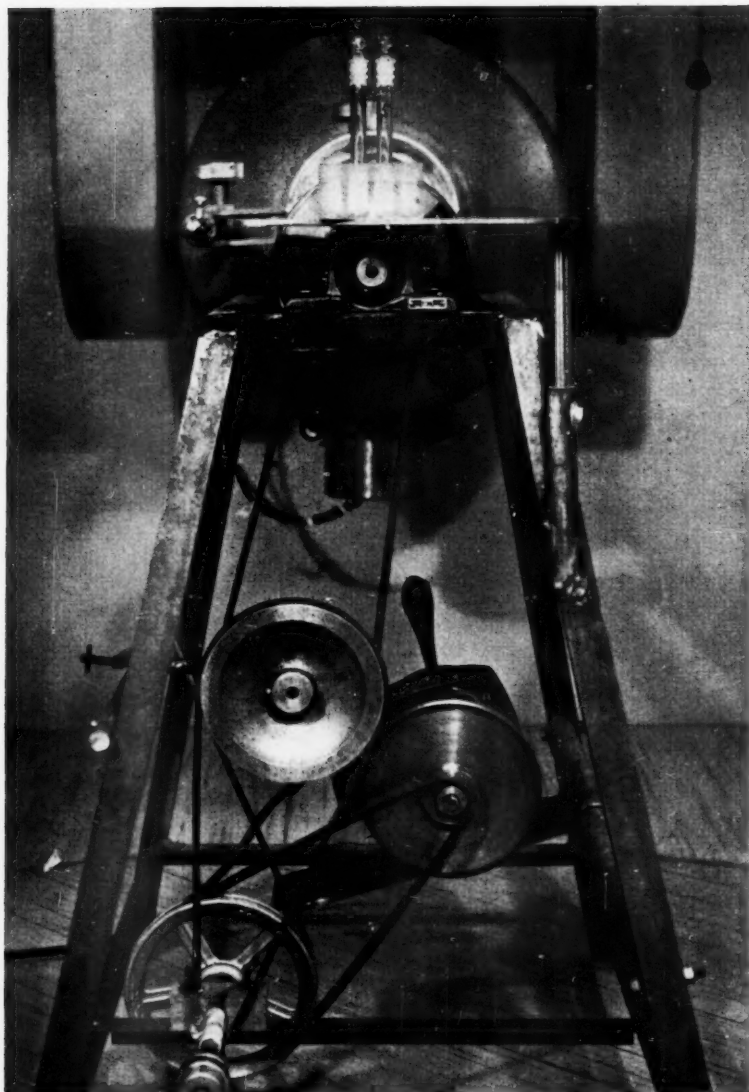
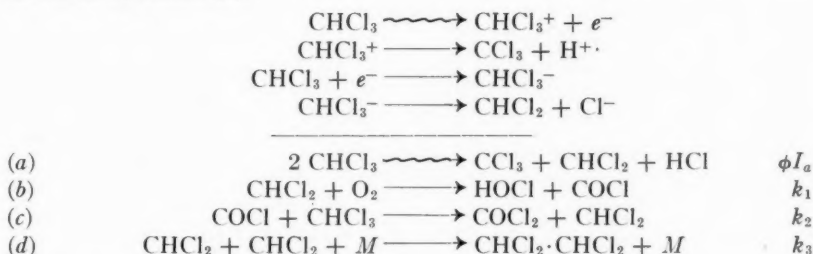


FIG. 7. Rotating sector apparatus and 1000 c.  $\text{Co}^{60}$  source.



the results reported here, since the over-all acid yield has been found to be inversely proportional to the square root of the radiation intensity, meaning that a recombination process, second order with respect to the radicals important to the chain propagation reaction, must be the principal process by which those radicals disappear (4, p. 197).

The following sequence of reactions leads to a kinetic expression in accord with the observed results. The products, HCl, HOCl, and  $\text{COCl}_2$  have been identified by others (2).



where  $M$  is any nonreacting molecule in the system.

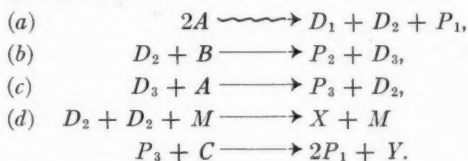
A chain reaction involving  $\text{CHCl}_2$  and  $\text{O}_2$  has been given since  $\text{O}_2$  is known to promote the production of acid on irradiation, and since the reaction

$\text{CCl}_3 + \text{CHCl}_3 \longrightarrow \text{Cl} + \text{CCl}_3 \cdot \text{CHCl}_2 \quad \Delta H = -2 \text{ kcal./mole}$   
 followed by  $\text{Cl} + \text{CHCl}_3 \longrightarrow \text{HCl} + \text{CCl}_3 \quad \Delta H = +4.6 \text{ kcal./mole}$   
 is not so probable on the basis of  $\Delta H$  values, those for reactions (b) and (c) being  $-52$  and  $-2 \text{ kcal./mole}$ , respectively. The  $\Delta H$  values have been taken from Ref. (2).

The phosgene reacts with water to give HCl and  $\text{CO}_2$ , i.e.,



Letting  $A = \text{CHCl}_3$ ,  $D_1 = \text{CCl}_3$ ,  $D_2 = \text{CHCl}_2$ , etc., the above equations can be written:



Assuming steady state conditions, an expression for  $D_2$  can be obtained, i.e.:  $dD_2/dt = \phi I_a - k_1 D_2 B + k_2 D_3 A - 2k_3 D_2^2 M = 0$

and  $dD_3/dt = k_1 D_2 B - k_2 D_3 A = 0$ ,

so that  $\phi I_a = 2k_3 D_2^2 M$ ,

and finally,  $D_2 = (\phi I_a / 2k_3 M)^{1/2}$ .

The rate of acid production,  $dP/dt$ , where  $P = P_1 + P_2 + P_3$ , is given by  $dP/dt = \phi I_a + k_1 D_2 B + 2K_2 D_3 A$ .

Since  $k_2 D_3 A = k_1 D_2 B$ , then

$$\begin{aligned}
 dP/dt &= \phi I_a + 3k_1 D_2 B \\
 &= \phi I_a + 3k_1 B \cdot (\phi I_a / 2K_3 M)^{1/2}.
 \end{aligned}$$

By dividing through by  $I_a$  the over-all quantum yield is obtained,

$$\Phi = \phi + 3k_1B \cdot (\phi/2k_3I_aM)^{\frac{1}{2}}.$$

The quantity  $\Phi$  of this expression is proportional to the  $S$  of Fig. 5, and  $I_a$  is proportional to  $R$ . It is seen that the expression obtained for  $\Phi$  is in accord with the observed results. The intercept on the  $S$  axis of Fig. 5 is proportional to the primary quantum yield,  $\phi$ , which here will be the number of chloroform molecules disrupted (by loss or gain of an electron followed by subsequent dissociation to give a free radical) as a result of ionizations produced by interaction of one photon with an electron (primary electron). Since the primary electron may, by collisional processes, produce many secondary electrons, all causing varying amounts of ionization, the primary quantum yield may be very high.

The rotating sector experiments with chloroform are important here mainly in showing that the average lives of the free radical chains are much greater than the time between the pulses of X rays emitted from the betatron. This could also be deduced from Fig. 5 ( $S$  vs.  $R^{-\frac{1}{2}}$ ), which shows that the specific acid yields are approximately the same with  $\text{Co}^{60}$  gamma-rays and betatron X rays. For a radiation-initiated reaction whose measured rate is not directly proportional to the intensity, the effect of pulsed radiation may be important. Dickinson (4; see also Ref. 1) has given a detailed treatment of the theory of the effects of intermittent radiations. If the rate with continuous irradiation is  $kI_0^n$ , the rate with intermittent radiations will be either  $r k I_0^n$  or  $k(r I_0)^n$ , depending on whether the intermittency is slow or fast (or the dark periods long or short compared with the average life of the rate-controlling intermediates). The transition between the two cases occurs when the dark periods are of the same order as the average life of the intermediates (4, p. 203). Here  $r$  is the ratio of the length of the light period to that of the sum, dark period plus light period, and  $n$  is the power of the intensity on which the reaction rate is found experimentally to depend. For betatron radiations emitted in four-microsecond pulses every 1/180th sec.,  $r = 7.19 \times 10^{-4}$  and  $n = 0.5$ . Also the average dose rate during a pulse, corresponding to  $I_0$ , is  $I_m/7.19 \times 10^{-4}$ , where  $I_m$  is the measured dose rate. Now, if the average life of the intermediates is less than 1/180 sec., corresponding to a long dark period, the rate will be given by

$$7.19 \times 10^{-4} \cdot k \cdot (I_m/7.19 \times 10^{-4})^{0.5} = 0.0268 \cdot k \cdot I_m^{0.5},$$

while if the average life is greater than 1/180 sec. the rate will be given by

$$k(7.19 \times 10^{-4} \cdot I_m/7.19 \times 10^{-4})^{0.5} = k \cdot I_m^{0.5}.$$

Thus, the rate of acid production, using the measured dose rate as a criterion, should be the same with both betatron and  $\text{Co}^{60}$  radiations provided the average life of the rate-controlling intermediates is greater than 1/180 sec. The rotating sector experiments with  $\text{Co}^{60}$  gamma-rays showed that the average chain lifetime, at  $I_0 = 1200 \text{ V/hr.}$ , is about one second. The observed similarity of specific acid yields obtained with intermittent betatron X rays and continuous  $\text{Co}^{60}$  gamma-rays is therefore consistent with the theory outlined briefly above.

The results obtained with  $\text{Co}^{60}$  gamma-rays and betatron X rays do not seem to depend on the energies of the radiations. The difference in the positions of the two lines in Fig. 5 probably is not due to the differences in energy, since the percentage difference due to energy dependence, if any, should not increase with increasing dose rate. The difference may be due to breakdown in the dependence of specific yield on  $(\text{dose rate})^{-\frac{1}{2}}$  at the very high dose rates such as are obtained during a betatron pulse. The free radical concentrations may then be so high that several chain-termination reactions may become important.

#### ACKNOWLEDGMENTS

We are grateful to the Defence Research Board of Canada for financial assistance (D.R.B.X-16) and to the Saskatchewan Cancer Commission for use of the betatron, and kilocurie  $\text{Co}^{60}$  unit. One of us (R.W.H.) is holder of a National Research Council Studentship.

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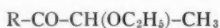
# THE ETHANOLYSIS OF 3-HYDROXY-1-(4-HYDROXY-3-METHOXYPHENYL)-2-PROPANONE IN RELATION TO LIGNIN CHEMISTRY<sup>1</sup>

By J. A. F. GARDNER

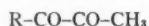
## ABSTRACT

The ketol, 3-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone, was subjected to ethanolysis and found to yield the four propylphenols which can be isolated from the ethanolysis products of isolated conifer lignin and of conifer lignin *in situ*. The significance of this finding is briefly discussed.

In the period 1939-1943, a careful investigation of the water soluble phenolic products from the ethanolysis of extractive-free spruce-wood by Hibbert and co-workers (5, 7, 18, 26) resulted in the isolation and identification of four propylphenols, 2-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone (I), 1-(4-hydroxy-3-methoxyphenyl)-1,2-propanedione (II), 1-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone (III), and 1-(4-hydroxy-3-methoxyphenyl)-2-propanone (IV).



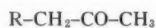
I



II



III



IV

R = 4-hydroxy-3-methoxyphenyl

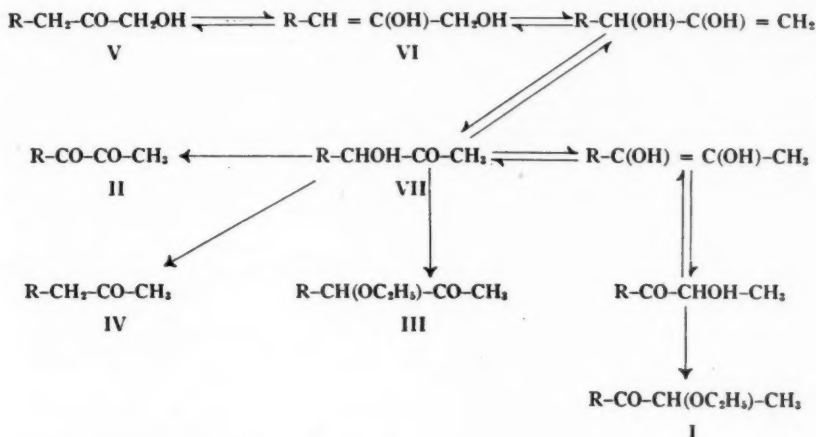
From maple-wood, in addition to these, the syringyl (R = 4-hydroxy-3, 5-dimethoxyphenyl) analogues were isolated. The total yield of pure identified products based upon the original Klason lignin of the wood was approximately 5 per cent for spruce-wood and approximately 10 per cent for maple-wood. In spite of the low yields, these findings were of considerable significance in that they provided some direct evidence for the theory that lignin is derived from propylphenol monomers.

In view of the absence of primary alcoholic or terminal ether groups in these products and the evidence for the presence of such groups in lignin provided by analytical results (4) and by the isolation of 3-cyclohexyl-1-propanols from the products of high pressure hydrogenation (3, 12, 15), Hibbert (16) suggested that the propylphenols I-IV were derived from a more reactive  $\beta$ -hydroxyconiferyl alcohol (VI) type of structural element by means of a series of interconversions:

<sup>1</sup> Manuscript received January 27, 1954.

Contribution from Vancouver Laboratory, Forest Products Laboratories of Canada, Forestry Branch, Department of Northern Affairs and National Resources, Canada.

Presented before the Western Regional Conference, Chemical Institute of Canada, Saskatoon, October 24-25, 1952.



This concept was consistent with the absence of  $\text{C-CH}_3$  groups in lignin *in situ* as determined by chromic acid oxidation in contrast to their presence in the ethanolysis products and isolated lignins (22). Convincing experimental evidence that such a series of interconversions was capable of yielding the ethanolysis products was provided by extensive studies of the analogous ketols in the veratryl ( $\text{R} = 3,4\text{-dimethoxyphenyl}$ ) series (8, 10), and of the diacetate of VII in the guaiacyl series (23). Ethanolysis of the diacetate of VII using the conditions employed on wood yielded the same four propylphenol products, I-IV. A study of the ketol, 3-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone (V), for final proof that it or its enol (VI) could yield the propylphenols (I-IV) by ethanolysis was delayed by difficulties in its synthesis which was finally achieved by Fisher and Hibbert (9).

The ethanolysis of V has now been accomplished. Using the conditions employed on wood, the product was a mixture of the propylphenols, I-IV, and a petroleum ether ( $30\text{--}60^\circ$ ) insoluble polymer in yields of 26, 9, 4.5, 2, and 20% respectively. This result and the isolation of the same propylphenols by ethanolysis of lignin *in situ* and of extracted lignins such as periodate lignin (24), hydrochloric acid lignin (14), and Brauns' "native" lignin (11) provide strong evidence for the presence in the lignin complex of the side chain  $\text{-CH}_2\text{-CO-CH}_2\text{OH}$  or its enol form.

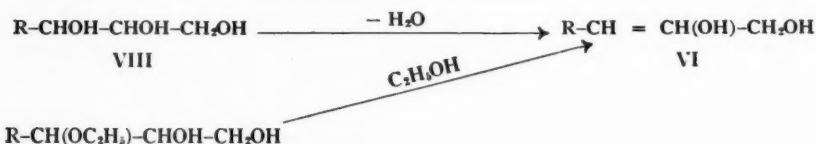
The presence in lignin of this side chain as an inner structural element readily freed by hydrolysis would be consistent with other properties of lignin *in situ*. Important examples already noted are the presence in the side chain of primary alcohol and ether groups and the absence of end methyl groups. Rearrangement of the side chain under the influence of a variety of reagents as demonstrated previously (8, 10) and in this work would account for the presence of end methyl groups in isolated lignins. This tendency to rearrange might also account to some extent for the apparent inconsistencies

in the literature of lignin concerning the content of other constituent groups such as secondary and tertiary hydroxyls (4).

The theory that the sulphonatable groups of lignin are benzyl alcohols or ethers was originally proposed by Holmberg (17) on the basis of experiments with model compounds. The strong support for this theory provided by the investigations of many others on the sulphonation reactions of lignin and model compounds has been reviewed recently by Lindgren (21). The possibility exists that hydroxyconiferyl alcohol might undergo similar sulphonation reactions by virtue of rearrangement to the benzyl alcohol derivative, VII, as in ethanolysis. This possibility will be explored.

Shorygina and co-workers (25) have provided some additional evidence that hydroxyconiferyl alcohol occurs as a structural element in lignin. By treating cuprammonium lignin with sodium in liquid ammonia, these workers obtained 1-(4-hydroxy-3-methoxyphenyl)-2-propanol in a yield of 12%. They interpreted this result as indicating that the basic structural element in lignin is  $\beta$ -hydroxyhydroconiferyl alcohol or  $\beta$ -hydroxyconiferyl alcohol (VI), the latter being more likely.

No indisputable evidence for the presence of carbonyl groups in lignin *in situ* is available although their presence has been suggested by a number of workers and small amounts have been detected in some isolated lignins (13). If hydroxyconiferyl alcohol groups or structural elements capable of giving rise to such groups are present to any great extent in lignin it is evident that the carbonyl function is hindered or masked in some way by the mode of linkage between elements. Since the experimental portion of this paper was completed, Adler and Yllner (1) have reported on the reactions of veratrylglycerol in relation to lignin chemistry. The results of their experiments on ethanolysis make it evident that a propylphenol containing no ketonic group such as guaiacylglycerol (VIII) is also capable of giving rise to the lignin ethanolysis products via  $\beta$ -hydroxyconiferyl alcohol, VI. They suggested that this alcohol might be formed either by a primary dehydration or by loss of ethanol from an ethyl ether:



It may be significant that, as shown in Table I, the yields of monomeric oils from ethanolysis of isolated lignins and lignin *in situ* are roughly one fifth of those obtained from ethanolysis of the ketol, V. If the ethanolysis oils from lignin were assumed to be derived only from one of the phenylpropane building elements, these yields could be taken as an indication that there are approximately five phenylpropane building elements in the average lignin building unit. Considerable evidence favoring an average unit molecular weight in this range is available in the lignin literature (4).

TABLE I  
TOTAL YIELDS OF MONOMERIC ETHANOLYSIS PRODUCTS FROM VARIOUS LIGNINS AND THE KETOL, V

Starting material	Yield, %	Reference
Spruce sapwood (extractive-free)	10*	26
Spruce periodate lignin	11.5	24
Spruce hydrochloric acid lignin	11	14
Spruce "native" lignin (Brauns)	10	11
3-Hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone (V)	50	..

\*Based on Klason lignin.

## EXPERIMENTAL

The pure ketol, V, was a colorless crystalline solid, melting point 85–86°, semicarbazone melting point 147–148° (Fisher and Hibbert reported 81–82° and 147–148° respectively). It was slightly unstable at room temperature and gradually acquired a faint vanillin-like odor and a melting point in the 80–83° range which probably accounts for the low melting point previously reported. Paper chromatographic experiments on a preparation kept a year in the laboratory indicated that vanillin was the contaminant. Only minor changes were made in the method of synthesis from vanillin reported by Fisher and Hibbert (9). Much time was saved by acetylating homovanillic acid by the Chattaway method (6), instead of by boiling for six hours with acetic anhydride, and high yields (90%) of pure product were obtained.

*Acetylation of Homovanillic Acid*

Homovanillic acid (12.95 gm.) in aqueous sodium hydroxide solution (7.62 gm. in 13 cc.) was treated with crushed ice (40 gm.) and then acetic anhydride (9.5 cc.). The mixture was agitated vigorously for two minutes before acidification with 6 *N* hydrochloric acid (34 cc.) which precipitated the acetate as white fluffy crystals. The product was filtered, washed with water, and dried. Yield 14.5 gm. (92%), melting point 138–139°C.

*Ethanolysis of 3-Hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone, V*

Two ethanolyses were run using the same technique as described by Mitchell and Hibbert (23). In the first trial experiment on a small sample (2.045 gm.), after paper chromatography had indicated the presence of the products, I–IV, in the petroleum ether (30–60°) soluble oil (1.02 gm.), it was possible to isolate and identify the two main products, I and II. For the isolation of the small quantities of III and IV produced, the petroleum ether soluble oil (3.9 gm.) obtained from a second ethanolysis of a larger quantity of V (8 gm.) was used.

*Paper Chromatography*

Samples of the various fractions and isolates were resolved on Whatman No. 1 filter paper concurrently with synthetic reference samples and mixtures. Solvent systems such as petroleum ether (65°–110°) – water (2:1), diethyl

\*Melting points were determined on Fisher-Johns melting point apparatus and are uncorrected.



ether - conc. ammonium hydroxide - water (4:1:1), and butanol - conc. ammonium hydroxide (4:1) were found to be useful. With the butanol - ammonium hydroxide solvent it was possible to resolve mixtures of all four propylphenols and vanillin, the approximate  $R_f$  values at 25° being: I, .66; II, .51; III, .79; IV, .87; and vanillin, .44. For detection the ferric chloride - potassium ferricyanide reagent of Barton (2) was used.

*Isolation of 2-Ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone, I*

After extraction of the bisulphite-soluble fraction with sodium bisulphite the so-called "phenol" fraction (26) was treated with anhydrous ammonia in ether to precipitate the crystalline ammonium salt of I (0.57 gm.). Yield on the ketol was 26%. Methylation of the ammonium salt with dimethyl sulphate gave the crystalline methyl ether. Melting point and mixed melting point with synthetic 2-ethoxy-1-(3,4-dimethoxyphenyl)-1-propanone and an authentic sample isolated from the ethanolysis of western hemlock-wood were identical.

*Isolation of 1-(4-Hydroxy-3-methoxyphenyl)-1,2-propanedione, II*

The oil (0.325 gm.) recovered from the bisulphite-soluble portion was treated in aqueous solution with hydroxylamine and nickel salts as described previously (18) to give the red nickel glyoxime salt of the diketone. Yield - 0.222 gm. (equivalent to a 9% yield of diketone). Hydrolysis gave II, melting point 69-70°, which gave a quinoxaline, melting point 160-161°. Both II and its quinoxaline showed no mixed melting point depression with authentic samples.

*Isolation of 1-(4-Hydroxy-3-methoxyphenyl)-2-propanone, IV*

The second ethanolysis experiment (on 8.0 gm. of VI) gave a petroleum ether soluble oil (3.9 gm.) which was separated into a bisulphite-soluble fraction, A, and a "phenol" fraction, B, as before.

Removal of the diketone, II, from A and hydrolysis (20) of the residual oxime gave an oil (0.238 gm.) which paper chromatograms indicated to be IV. Distillation (150-160° at 2 mm.) gave a light yellow oil,  $n_D^{25}$  1.548, 0.16 gm. (2%), from which the semicarbazone, melting point 154-155°, and the thio-semicarbazone, melting point 188-189°, were prepared. A synthetic sample (20),  $n_D^{25}$  1.547, gave the same yield of the same derivatives. There were no mixed melting point depressions.

*Isolation of 1-Ethoxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone, III*

The "phenol" fraction B (2.59 gm.) gave paper chromatograms indicating the presence of I and III. After removal of I as the ammonium salt, the residual oil (0.515 gm.), which with several solvent systems gave paper chromatograms indicating it to be III, was distilled (160-180°, 0.5 mm.). Yield, 0.363 gm. of a partially crystalline oil. The semicarbazone (0.08 gm. from 0.17 gm.), melting point 170-171°, gave no mixed melting point depression with the semicarbazone (prepared in similar yield) of a synthetic sample (19), melting point 170-171°.

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# THE SYNTHESIS OF 4-DIALKYLAMINOETHYLPYRIDINES<sup>1</sup>

BY ANTHONY J. MATUSZKO<sup>2</sup> AND ALFRED TAURINS

## ABSTRACT

For the synthesis of 4-dialkylaminoethylpyridines two reactions were employed, namely, the Mannich condensation of 4-methylpyridine with formaldehyde and secondary amines, and the addition of secondary amines across the double bond of the 4-vinylpyridine. In the first reaction with diethyl-, di-isopropyl-, di-*n*-butylamine, pyrrolidine, and morpholine, normal Mannich bases (IV-VIII) were obtained. The unsaturated bases (X, XI) were the reaction products when dimethylamine and piperidine were used. The addition of those products 1,3-bis-(dialkylamino)-2-(4'-pyridyl)-propanes (XII, XIII) were formed when dimethyl- and diethylamine were applied.

The structures of the normal Mannich bases were confirmed by the synthesis of several compounds (III, IV, VII-IX) from 4-vinylpyridine and secondary amines.

## INTRODUCTION

The Mannich condensation of methylpyridines and -quinolines has been studied only with the substances containing methyl group in the 2-position. Héou-Féou (7) investigated the reaction of 2-methylpyridine with formaldehyde and diethylamine and with formaldehyde and piperidine. The condensation of 2-methylquinoline has been reported by Kermack and Muir (8), Ger. Pat. 497, 907 (5), Héou-Féou (6), and Boekelheide and Marinetti (1). The Mannich procedure has been recently applied by Sommers, Freifelder, Wright, and Weston (11) to prepare some derivatives of 2-methylpyridine and -quinoline.

The objective of this work was to investigate the reactivity of the methyl group in the 4-position of the pyridine ring in the Mannich condensation and to synthesize certain 4-dialkylaminoethylpyridines. Since similar compounds could be obtained by the addition of secondary amines across the double bond of the 4-vinylpyridine we applied this reaction to confirm the structures of the products obtained in the Mannich reaction.

The addition of nucleophilic reagents with active hydrogen, like secondary amines, to 2- and 4-vinylpyridines was postulated by Doering and Weil (2). They condensed only 2-vinylpyridine with diethylamine, and piperidine, respectively. Similar condensations of 2-vinylpyridine have been carried out using morpholine and 1-methylpiperazine as secondary bases (11). The addition of ketones to 2-vinylpyridine has also been studied by Levine and Wilt (9), and Wilt and Levine (12).

## DISCUSSION

The principal product from the condensation of dimethylamine hydrochloride with formaldehyde and 4-methylpyridine (I) was not the normal Mannich base, 4-( $\beta$ -dimethylaminoethyl)-pyridine (III), but the unsaturated

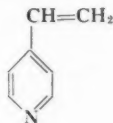
<sup>1</sup> Manuscript received January 6, 1954.

Contribution from the Organic Chemistry Laboratory, McGill University, Montreal, Quebec, with the financial assistance of the National Research Council of Canada, Ottawa.

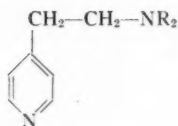
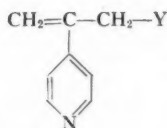
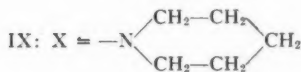
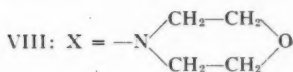
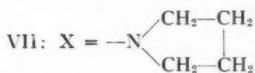
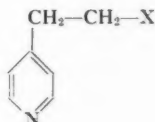
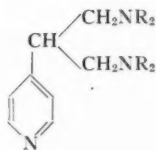
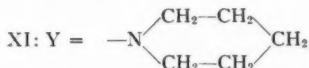
<sup>2</sup> Present address: Department of Chemistry, La Fayette College, Easton, Pa.



I



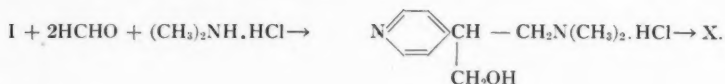
II

III: R = CH<sub>3</sub>IV: R = C<sub>2</sub>H<sub>5</sub>V: R = i-C<sub>3</sub>H<sub>7</sub>X: Y = N(CH<sub>3</sub>)<sub>2</sub>XII: R = CH<sub>3</sub>XIII: R = C<sub>2</sub>H<sub>5</sub>

## Formulae Scheme

base, 4-( $\alpha$ -methylene- $\beta$ -dimethylaminoethyl)-pyridine (X). This was substantiated by analyses of X and its chemical behavior. The sample of X was obtained by distillation as a colorless oil which showed a high degree of unsaturation and turned reddish-brown on standing even in a closed container. The terminal methylene group  $>\text{C}=\text{CH}_2$  of the X was determined by ozonolysis according to the method given by Doeuvre (3, 4) and modified by Naves (10). This method is by no means quantitative, therefore it was possible to detect the cleavage of the methylene group to produce formaldehyde to the extent of 34%. The sample of III was prepared by the addition of dimethylamine to the ethylene double bond of the 4-vinylpyridine (II), and it did not show any formation of formaldehyde in the reaction of ozonolysis.

The formation of the methylene base X presumably goes through the methylol compound which loses a molecule of water either by the interaction of a base, or during the vacuum distillation:



The highest yield (45%) of X was obtained when the reaction mixture contained two moles of formaldehyde for one mole of I and dimethylamine. The variation of the reaction time (6–24 hr.) and temperature (50–100°) did not give any indication of formation of III in this reaction. However, the prolonged reaction time of 24 hr. at 60° gave in addition to X a higher boiling compound, 1,3-bis(dimethylamino)-2-(4'-pyridyl)-propane (XII).

The unsaturated methylene base, 4-( $\alpha$ -methylene- $\beta$ -piperidylethyl)-pyridine (XI) was obtained as the only reaction product in the Mannich condensation of piperidine, formaldehyde, and I. Since piperidine reacted with 4-vinylpyridine to give 4-( $\beta$ -N-piperidylethyl)-pyridine (IX) it was possible to compare both of the derivatives of piperidine formed in two different reactions. The presence of the methylene group  $>\text{C}=\text{CH}_2$  in XI was detected by the Doeuve reaction (3, 4) which produced 28% formaldehyde.

In the Mannich condensation I reacted normally with formaldehyde and diethyl-, di-isopropyl-, and di-*n*-butylamine, respectively, to give the corresponding 4-dialkylaminoethylpyridines IV, V, and VI, in low yields. Pyrrolidine and morpholine reacted with I and formaldehyde in a similar manner to yield the bases VII and VIII.

The condensation of 4-vinylpyridine and dimethylamine was carried out by heating a water solution containing both components in molar ratio 1:2 for 24 hr. at 90°. Although the 4-vinylpyridine was not completely soluble in water, enough of it was dissolved at 90° to react with dimethylamine. The yield of 4-( $\beta$ -dimethylaminoethyl)-pyridine (III) was 40% of the theoretical. A similar procedure was applied in the interaction of 4-vinylpyridine with diethylamine. When the reaction was carried out at reflux temperature for 48 hr., the yield of IV was increased to 70%.

Doering and Weil reported that the reaction of 2-vinylpyridine and diethylamine in the absence of any solvent in a sealed tube gave a poor yield of the 2-( $\beta$ -diethylaminoethyl)-pyridine. The good yield of IV which we obtained in water solution indicated that a water solvent was favorable for the reaction.

Successful condensation of 4-vinylpyridine was carried out with pyrrolidine, morpholine, and piperidine to obtain the products VII, VIII, and IX. The reaction occurred when the corresponding components were mixed and refluxed for six hours in the absence of water.

Although it was not in the realm of this investigation to study the physiological activity of the compounds prepared, an observation was made which proved to be of interest. Twenty-four hours after performing a series of dis-

tillations of the Mannich bases, reddening of certain areas of the face and hands of the worker was observed. This reddening was similar to a caustic burn and it was followed by blistering which continued for five to six days. Once the blistering had subsided and the exposed areas had healed, scars remained which were noticeable even six months later. The reddening and blistering appeared to be similar to that of the shingles, a virus infection. It was not discovered which particular compound caused this behavior, since a number of distillations were carried out at this time.

#### EXPERIMENTAL\*

In the experimental part the Mannich condensation is denoted as the Procedure A and the reaction of 4-vinylpyridine with amines as the Procedure B.

##### *4-( $\alpha$ -Methylene- $\beta$ -dimethylaminoethyl)-pyridine (X)*

A mixture of 4.7 gm. (0.05 *M*) of 4-methylpyridine (1) and 8.2 gm. (0.01 *M*) of dimethylamine hydrochloride was heated to 95–100° while 8.5 gm. of 30% formaldehyde was added with stirring over a period of one hour. The reaction was continued for five additional hours. The reaction mixture was cooled, made alkaline with potassium carbonate, and extracted with ether. The ether solution was dried over anhydrous sodium sulphate and the ether evaporated at reduced pressure. Distillation of the residue yielded 3.5 gm. (43% of the theoretical) of a colorless liquid, boiling point 65–66° at 0.5 mm.;  $n_D^{24}$  1.5170. Anal. calc. for  $C_{10}H_{14}N_2$ : C, 74.01; H, 8.71%. Found: C, 73.83; H, 8.44%.

The *dipicrate* of *X* was prepared in ethanol solution and after recrystallization from the same solvent was obtained in the form of orange-yellow needles, melting point 147–148°. Anal. calc. for  $C_{22}H_{20}N_8O_{14}$ : C, 42.70; H, 3.26; N, 18.13%. Found: C, 43.01; H, 3.28; N, 18.45%.

The *monopicate* of *X* was obtained using a smaller ratio of picric acid and was obtained from water as yellow crystals, melting point 124–125°. Anal. calc. for  $C_{16}H_{17}O_7N_3$ : N, 17.65%. Found: N, 17.82%.

##### *Determination of the Terminal Methylene Group $>C = CH_2$ (3, 4)*

A solution containing 250 mgm. of the *X* in 5 ml. of a mixture (3:2) of ethylacetate and glacial acetic acid was cooled to –15° and treated with ozone for three minutes. One-half milliliter of the ozonized solution was added to a mixture of 30 ml. Grosse-Bohle reagent, 15 ml. hydrochloric acid, and 45 ml. water. After the mixture was shaken and made up to 100 ml., the volumetric flask was stoppered and the mixture allowed to stand for six hours at room temperature. Meanwhile 2 ml., 1 ml., and 0.5 ml. samples of a 0.120% solution of formaldehyde was treated with the Grosse-Bohle reagent and water and diluted to 100 ml. as above. Comparative visual colorimetric tests indicated that in the ozonolysis of *X* the terminal methylene group had been transformed to formaldehyde to the extent of 34%.

\*Microanalyses by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.



*1,3-Bis(dimethylamino)-2-(4'-pyridyl)-propane (XII)*

A mixture of 40.5 gm. (0.5 *M*) of I, 40.7 gm. (0.5 *M*) of dimethylamine hydrochloride, 45 gm. of 35% formaldehyde, and 30 ml. of water was stirred at 58° for 24 hr. The further steps in the procedure were similar to those described previously. The residue yielded 20 gm. of X and 5.5 gm. of XII in the form of a colorless oil, boiling point 84–88° at 0.5 mm.;  $n_D^{24}$  1.4998. The yield was 10.8% of the theoretical on the basis of the amount of the amine salt used. Anal. calc. for  $C_{12}H_{21}N_3$ : C, 69.50; H, 10.22%. Found: C, 69.30; H, 9.92%.

The *tripicrate* of XII was prepared in ethanol and recrystallized from acetone in the form of yellow plates; m.p. 171–172°. Anal. calc. for  $C_{30}H_{30}N_{12}O_{21}$ : C, 40.24; H, 3.38; N, 18.79%. Found: C, 40.01; H, 3.42; N, 18.93%.

*4-(β-Dimethylaminoethyl)-pyridine (III)*

A mixture containing 36 gm. of 25% aqueous solution of dimethylamine and 10.5 gm. of 4-vinylpyridine (II) was stirred at 90° for 24 hr. II was not completely miscible with water. The reaction product was extracted with ether, the ether extract dried over anhydrous sodium sulphate, evaporated and distilled at reduced pressure. The yield of III was 6 gm. (40%); boiling point 63–64° at 0.5 mm.;  $n_D^{24}$  1.5023. Anal. calc. for  $C_9H_{14}N_2$ : C, 71.94; H, 9.40%. Found: C, 72.15; H, 9.60%.

The *dipicrate* of III was prepared in ethanol and recrystallized from acetone; m.p. 159–160°.

*4-(β-Diethylaminoethyl)-pyridine (IV)*

*Procedure A.*—Glacial acetic acid (22 gm.) was added dropwise to a mixture of 9.3 gm. (0.1 *M*) of I, 7.3 gm. (0.1 *M*) of diethylamine, and 8.5 gm. of 35% formaldehyde. The reaction mixture was stirred at 60° for 10 hr., made alkaline with 20% potassium carbonate solution, and extracted with several portions of chloroform. The IV was obtained as a colorless liquid, boiling point 80–81° at 0.5 mm.;  $n_D^{24}$  1.4913. The yield of IV was 2.3 gm. (14%). Anal. calc. for  $C_{11}H_{18}N_2$ : C, 74.09; H, 10.18%. Found: C, 74.27; H, 10.05%.

The *dipicrate* of IV was crystallized from water as yellow crystals, melting point 146–147°. Anal. calc. for  $C_{23}H_{24}N_8O_{14}$ : C, 43.37; H, 3.80; N, 17.61%. Found: C, 43.25; H, 3.85; N, 17.69%.

The *monopicrate* of IV was recrystallized from water and obtained in the form of yellow crystals, melting point 109–110°. Anal. calc. for  $C_{17}H_{21}N_5O_7$ : N, 17.11%. Found: N, 17.02%.

*Procedure B.*—A solution of 14.6 gm. (0.2 *M*) of diethylamine in 30 ml. water was heated to reflux together with 10.5 gm. (0.1 *M*) of 4-vinylpyridine for 48 hr. The ether extract gave 12.5 gm. (70%) of IV, b.p. 80° at 0.5 mm. The *dipicrate* of IV melted at 146–147° and the mixed melting point of it was not depressed by the *dipicrate* of IV obtained in the Procedure A.

*1,3-Bis(diethylamino)-2-(4'-pyridyl)-propane (XIII)*

A mixture consisting of 54.8 gm. (0.5 *M*) diethylamine hydrochloride, 46.5 gm. (0.5 *M*) I, 45 gm. 35% formaldehyde, and 30 ml. water was stirred



at 60° for 24 hr. The chloroform extract yielded 10.5 gm. of IV, and 5 gm. of XIII (8.6%), an oil boiling at 98–100° at 0.5 mm.;  $n_D^{24}$  1.5089. Anal. calc. for  $C_{16}H_{29}N_3$ : C, 72.93; H, 11.10%. Found: C, 72.70; H, 10.78%.

The triplicate of XIII was prepared in ethyl alcohol and, after recrystallization from acetone, melted at 138–139°. Anal. calc. for  $C_{34}H_{38}N_{12}O_{21}$ : N, 17.68%. Found: N, 17.72%.

4-( $\beta$ -Diisopropylaminoethyl)-pyridine (V)

Formaldehyde (16 gm. of 35% solution) was added dropwise with stirring over a period of two hours to a mixture of 13.7 gm. of diisopropylamine hydrochloride and 18.6 gm. 4-methylpyridine. The temperature was kept at 95° and the reaction continued for an additional four hours. V was obtained as a colorless oil, boiling at 116° at 0.5 mm. The yield was 3 gm. (14%). Anal. calc. for  $C_{13}H_{22}N_2$ : C, 75.68; H, 10.75; N, 13.57%. Found: C, 75.40; H, 10.55; N, 13.60%.

4-( $\beta$ -Di-n-butylaminoethyl)-pyridine (VI)

A mixture of 16.3 gm. (0.1 M) of dibutylamine hydrochloride and 9.3 gm. (0.1 M) of 4-methylpyridine was heated to 92° and stirred while 8.5 gm. of 35% formaldehyde was added dropwise. The reaction was continued for 12 hr. VI was obtained as a colorless liquid, b.p. 111–113° at 0.5 mm. The yield was 2.3 gm. (10%). Anal. calc. for  $C_{15}H_{26}N_2$ : C, 76.86%; H, 11.18%. Found: C, 76.58%; H, 10.92%.

4-( $\beta$ -N-Pyrrolidylethyl)-pyridine (VII)

*Procedure A.*—A mixture consisting of 10.65 gm. (0.1 M) of pyrrolidine hydrochloride, 20 ml. water, 9.3 gm. (0.1 M) I was stirred at 80–85° while 9 gm. of 35% formaldehyde was added over a period of two hours and the reaction was continued for four hours. The ether extract gave 4 gm. (22%) of VII, an oil boiling at 93° at 0.5 mm. pressure. Anal. calc. for  $C_{11}H_{16}N_2$ : C, 74.95; H, 9.15; N, 15.90%. Found: C, 74.87; H, 8.95; N, 16.16%.

The dipicrate of VII was prepared in ethanol and after recrystallization from acetone, melted at 166°.

*Procedure B.*—Equimolar amounts (0.1 M) of pyrrolidine and 4-vinylpyridine was heated at 80–85° for six hours. The yield of VII was 14.5 gm. (83%). The substance had the boiling point 92–93° at 0.5 mm. Carbon, hydrogen, and nitrogen analyses gave results which were similar to those obtained in the analysis of the previous sample of VI. The dipicrate of VII (recrystallized from acetone) had the melting point 165–166°.

4-( $\beta$ -N-Morpholinylethyl)-pyridine (VIII)

*Procedure A.*—To a solution of 18.6 gm. (0.2 M) of I in 10 ml. of water was added 10.6 gm. (0.1 M) of morpholine hydrochloride in 10 ml. of water and 8.5 gm. of 35% formaldehyde. The addition was carried out over a period of two hours and the reaction was continued for four hours at 85–90°. VIII was obtained in the form of a colorless liquid, boiling point 117–119° at 0.5 mm. The yield was 3.5 gm. Anal. calc. for  $C_{11}H_{16}N_2O$ : C, 68.73; H, 8.39; N, 14.57%. Found: C, 68.55; H, 8.50; N, 14.38%.

*Procedure B.*—An equimolar (0.1 *M*) mixture of morpholine and 4-vinylpyridine was stirred at 105° for six hours. Distillation of the reaction mixture yielded 12.5 gm. (65%) of a colorless liquid, boiling point 116° at 0.5 mm. On cooling the oil solidified, giving crystals melting at 48–49°. Anal. calc. for  $C_{11}H_{16}N_2O$ : C, 68.73; H, 8.39%. Found: C, 69.02; H, 8.14%.

*4-(β-N-Piperidylethyl)-pyridine (IX)*

A mixture of 17 gm. (0.2 *M*) piperidine and 10.5 gm. (0.1 *M*) 4-vinylpyridine was heated to reflux (105°) for six hours and then fractionated in vacuum; 10.5 gm. (55%) of IX was obtained as a colorless liquid, b. p. 101° at 0.5 mm.;  $n_D^{24}$  1.5236. Anal. calc. for  $C_{12}H_{18}N_2$ : C, 75.73; H, 9.54%. Found: C, 75.72; H, 9.37%.

*4-(α-Methylene-β-piperidylethyl)-pyridine (XI)*

A mixture containing 4.7 gm. (0.05 *M*) of I, 12 gm. (0.1 *M*) of piperidine hydrochloride, and 8.5 gm. of 35% formaldehyde was heated under reflux for six hours. The ether extract gave 3.5 gm. (43%) of XI, which was a colorless oil, boiling at 105–106° at 0.5 mm. pressure;  $n_D^{24}$  1.5298. Anal. calc. for  $C_{13}H_{18}N_2$ : C, 77.17; H, 8.96%. Found: C, 76.97; H, 9.13%.

The ozonolysis of the XI in order to determine the terminal methylene groups indicated the formation of formaldehyde to the extent of 28%.

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## SYNTHESIS OF 1,2-DIALKYLHYDRAZINES AND THE CORRESPONDING AZOALKANES<sup>1,2</sup>

BY R. RENAUD AND L. C. LEITCH

### ABSTRACT

The limitations of present methods of synthesizing 1,2-dialkylhydrazines are discussed. A new method of obtaining these compounds in good yields by the reduction of azines with lithium aluminum hydride is reported. Lithium aluminum deuteride was employed as a tracer to investigate the mechanism of the reaction. The 1,2-dialkylhydrazines were oxidized to the azoparaffins in over 90% yields by mercuric oxide in water.

### INTRODUCTION

An important source of free radicals for kinetic investigations is the thermal or photochemical decomposition of azoalkanes (11). Up to now the availability of these compounds has been limited on account of the difficulty of obtaining the 1,2-dialkylhydrazines. For example, of the lower azoalkanes only the methyl and isopropyl compounds have long been known, azoethane having been prepared quite recently (15). This work was undertaken to develop a general method of preparing 1,2-dialkylhydrazines and thereby to provide a route to the required azocompounds.

Knorr and Köhler (9) obtained 1,2-dimethylhydrazine by alkaline hydrolysis of dimethylpyrazole and characterized it by means of several derivatives. It had previously been prepared by Harries and Klamt (6) by the methylation and subsequent hydrolysis of 1,2-diformylhydrazine, but their product was probably impure since it boiled over a wide range of temperature; furthermore, no derivatives were reported. The use of dibenzoyl-, instead of diformyl-, hydrazine is a later modification due to Folpmers (4). Hatt (7) subsequently developed the procedure into a useful though still very tedious method of preparing 1,2-dimethylhydrazine dihydrochloride. The over-all yield, which varies between 42 and 54%, is also low.

This route to 1,2-dialkylhydrazines was extended by Harries (5) who obtained 1,2-diethylhydrazine and a high boiling base by ethylation of 1,2-dibenzoylhydrazine and subsequent hydrolysis. The boiling point reported for 1,2-diethylhydrazine, viz. 84–86°C., is almost certainly wrong since Knorr and Köhler (*loc. cit.*) give the boiling point of the lower homologue, 1,2-dimethylhydrazine, as 80–81°C. In a recent paper, Weiniger and Rice (15) mention the preparation of 1,2-diethylhydrazine by ethylation of the copper derivative of 1,2-diformylhydrazine but the properties of the base and its derivatives are not recorded. It seems doubtful, therefore, whether pure 1,2-diethylhydrazine has ever been prepared in quantity.

The reductive alkylation of hydrazine with several aldehydes and ketones was very thoroughly investigated by Taipale (12, 13) during the early twenties

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as a general method of preparing 1,2-dialkylhydrazines. In general, ketones gave moderately good yields, but from aldehydes mixtures of the substituted hydrazines and large amounts of primary amines and ammonia were obtained. When the reaction was carried out in glacial acetic acid, the yields were still only moderate; in some cases the aldazines were rearranged to pyrazolines as had already been observed by Curtius and Zinkeisen (3). Simultaneously with the work of Taipale, the American workers Lochte, Bailey, and Noyes (10) reported the preparation of 1,2-diisopropylhydrazine by the reductive alkylation of acetone with hydrazine hydrochloride in water. More recently, Ugryumov (14) reported the preparation of 1,2-dibenzyl- and 1,2-diheptylhydrazine by the reductive alkylation of hydrazine with benzaldehyde and oenanthaldehyde respectively.

In the present work it was found that the reductive alkylation of acetaldehyde with hydrazine hydrochloride using hydrogen and Adam's catalyst gave a sirupy residue which yielded nothing crystalline besides ammonium chloride. It was then decided to prepare pure ethylideneazine by the method of Curtius and Zinkeisen (3) and to reduce it by the same method. The aldazine was prepared in excellent yield by condensing freshly distilled acetaldehyde and aqueous hydrazine. Reduction of the azine in water with platinum black gave a product which contained a large amount of ethylamine and distilled over a wide range of temperature. Oxidation of the reaction mixture with mercuric oxide in water gave a 20% yield of azobisethane, b.p. 56–58°C. When the reduction of the azine was carried out in the presence of carbon dioxide to maintain the pH of the reaction mixture at or near 7, the amount of ethylamine was considerably reduced but the yield of azobisethane obtained by oxidation was not improved. Reduction in glacial acetic acid gave a high boiling base which was probably the pyrazoline.

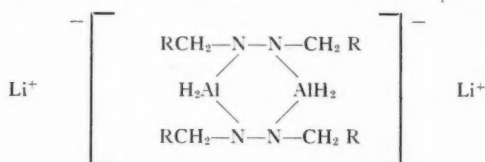
Reduction with Raney nickel alloy in dilute sodium hydroxide gave similar results. In fact, Beregi (1) described the preparation of amines by the hydrogenolysis of the azines of propionaldehyde and butyraldehyde with this alloy.

Since Class and Aston (2) recently reported the reduction of N,N-dimethyl-N'-methylene hydrazine to trimethylhydrazine with lithium aluminum hydride, it was thought ethylideneazine in particular, and azines in general, might be reduced in good yield by this method. The reduction product obtained from ethylideneazine was a base, b.p. 106–107°C. isolated in 80% yield. Its dihydrochloride melted at 168–169°C. and not at 160° as reported by Harries and Klamt (6); it analyzed correctly for diethylhydrazine dihydrochloride. The picrate could not be prepared in the normal way, but the picrolonate was readily obtained. The free base absorbs carbon dioxide from the air. Similarly, 1,2-diisopropylhydrazine was obtained from 2-propylidene azine and 1,2-*n*-propylhydrazine from 1-propylideneazine. The method could probably be extended also to higher homologues. Unfortunately, it is not applicable to the preparation of 1,2-dimethylhydrazine because the azine,  $\text{CH}_2=\text{N}-\text{N}=\text{CH}_2$ , could not be obtained from formaldehyde and hydrazine hydrate. An insoluble polymer was the only product isolable from this reaction.

Reduction of 1,2-diacetylhydrazine with lithium aluminum hydride would likewise lead to 1,2-diethylhydrazine. However, the sparing solubility of acylated hydrazines in solvents suitable for reactions with  $\text{LiAlH}_4$  prevented reduction in a reasonable time and the reactants were recovered unchanged.

The mechanism of the reduction of azines with lithium aluminum hydride was investigated by means of deuterated reagents. Ethylideneazine was reduced with ordinary lithium aluminum hydride and the complex decomposed by adding deuterium oxide; the 1,2-diethylhydrazine was isolated and oxidized to azobisethane by mercuric oxide in water. Mass spectrometric analysis indicated that the azobisethane contained no deuterium. In a second experiment ethylideneazine was reduced with lithium aluminum hydride containing 25% of the deuteride; the diethylhydrazine and azobisethane were isolated as before. The azobisethane now contained deuterium as shown by the appearance of strong peaks in its mass spectrum at 87 and 88 and a small peak at 89. Of course, the same results would have been obtained if exchange had occurred between the ethylideneazine and lithium aluminum deuteride. However, such an exchange was considered very unlikely since acetone and diacetyl, which contain labile hydrogen, undergo reduction to isopropyl-2-*d*-alcohol and 2,3-butanediol-2,3-*d*<sub>2</sub> without exchange with this reagent. Finally, dimethylketazine, which contains no hydrogen on the carbon atom adjacent to nitrogen, was converted into 2,2'-azobispropane by the same method. The mass spectrum of the product gave strong peaks at 115 and 116 corresponding to 2,2'-azobispropane with one and two deuterium atoms. The deuterium content was 42.4%.

These results may be explained by representing the complex by the formula



in which one mole of lithium aluminum hydride is utilized per mole of azine. The aluminum adds on to the nitrogen, and hydrogen to the carbon atom. This assumption was further justified by the observation that the 1,2-dialkylhydrazine is contaminated with the hydrazone when less than one mole of reducing agent is employed per mole of azine.

The oxidation of the 1,2-dialkylhydrazines to azoparaffins was best carried out by mercuric oxide suspended in water or ethanol. The yields of azobisethane, 1,1'-azobispropane, and 2,2'-azobispropane from the corresponding hydrazines were nearly quantitative. With 1,2-dimethylhydrazine, azomethane was obtained in 74% yield in contrast with the 25% yield obtained in this laboratory by cupric chloride oxidation of the hydrochloride (8). A further advantage of oxidizing the base with mercuric oxide in water is that the azomethane is free of methyl chloride which is a troublesome impurity in the product obtained by the other method.

## EXPERIMENTAL

*Ethylideneazine*

To a solution of 160 gm. (3.64 mole) of *freshly distilled* acetaldehyde in 400 ml. of ether in a 2 l. round-bottomed flask equipped with a stirrer, a separatory funnel, and a reflux condenser, a solution of 64% hydrazine in water, 92 ml. (1.9 mole), was added dropwise. The flask was immersed in ice-water during the addition of the hydrazine. The reaction mixture was stirred for 10 hr. at room temperature and then treated with 120 gm. anhydrous potassium carbonate in portions. The ether layer was separated, dried over anhydrous potassium carbonate, and distilled off. The residue, distilled through a 12 in. Stedman column, boiled at practically constant temperature, 95.5°C. The yield of colorless product,  $n_D^{20}$  1.4435,  $d_4^{26}$  0.813, was 134.3 gm. (88%).

*1,2-Diethylhydrazine*

Lithium aluminum hydride (30.0 gm. of 64% purity) was dissolved in 300 ml. of absolute ether in a 1 l. flask equipped with a stirrer, funnel, and reflux condenser. Ethylideneazine (50 ml.) was added dropwise with stirring to keep the ether refluxing. Stirring was continued under reflux for eight hours thereafter. The complex was decomposed by careful addition of aqueous 40% potassium hydroxide solution. The supernatant liquid was decanted from the inorganic salts into a funnel with a wad of glass wool. The residue was washed several times with small portions of ether. The combined ether filtrate was dried for several hours over pellets of potassium hydroxide, and siphoned into a dry flask for distillation. After the ether had been distilled off, the residue was fractionated through a Stedman column. A tube filled with ascariite was attached to the distilling assembly to prevent absorption of carbon dioxide from the air during distillation, which would cause the boiling point to fluctuate. After collecting a small forerun, b.p. 65–106°, 1,2-diethylhydrazine was collected between 106 and 107°C.,  $n_D^{20}$  1.4204,  $d_4^{26}$  0.797. The yield was 33.7 gm. (80%).

The picrate does not precipitate when equimolecular amounts of 1,2-diethylhydrazine and picric acid in ethanol are mixed. The picrolonate, m.p. 248–250°, after darkening at about 190°C., is readily prepared. The dihydrochloride melts at 168–169°C. Analysis of the dihydrochloride gave C, 29.95%, H, 8.6%. Calc. C, 29.81%, H, 8.7%. Mol. wt. (by iodine titration): Calc. 161, Found 160.2. Free base: Calc. 88.0, Found 87.5.

*1,2-Di-n-propylhydrazine*

1-Propylideneazine reduced in the same manner gave a 77.5% yield of 1,2-di-n-propylhydrazine, b.p. 149.5–150°C.,  $n_D^{20}$  1.4287,  $d_4^{26}$  0.7940. Hydrochloride, m.p. 175–175.5°C. Calc. for  $C_6H_{16}N_2 \cdot 2HCl$ , C, 38.2%; H, 9.53%. Found C, 39.3%, H, 10.17%. Mol. wt. (by iodine titration): Calc. 189.0. Found 188.76.

The picrolonate melted with decomposition at 243–244°C. after darkening at 191–192°C. Calc. for  $C_{16}H_{24}N_6O_5$ : C, 50.75%, H, 6.32%; N, 22.11%. Found: C, 50.86%; H, 6.35%; N, 22.4%.



*1,2-Diisopropylhydrazine*

This compound, which had been reported earlier by Lochte, Noyes, and Bailey (10), was obtained in excellent yield (81.4%) from 2-propylideneazine by the present method, b.p. 124–124.5°C.,  $n_D^{20}$  1.4160,  $d_4^{20}$  0.780. Mol. wt. (by iodine titration): Found 115.2. Calc. 116.

*Azobisethane*

A solution of 10.0 ml. of 1,2-diethylhydrazine in 40 ml. of water was added dropwise to a stirred suspension of 26.0 gm. of yellow mercuric oxide in 40 ml. of water in a flask with a short fractionating column and still head. The reaction mixture was slowly brought to a boil. After an azeotrope of azoethane and water had been collected between 53 and 58°C., the temperature rapidly rose to 90°C., and the distillation was stopped. The yield of product after drying over calcium chloride and distilling off the azoethane on a vacuum manifold was 9.4 ml. (97%), b.p. 58.0°C.,  $n_D^{20}$  1.3852.

*1,1'-Azobispropane*

This compound was prepared by the same method from 1,2-di-*n*-propylhydrazine. B.p. 113.5°C.,  $n_D^{20}$  1.4053. Yield: 88%.

*2,2'-Azobispropane*

This compound was prepared from 1,2-diisopropylhydrazine. B.p. 88.5°C.,  $n_D^{20}$  1.3899. Yield: 90%.

*Azomethane*

To a suspension of 75 gm. yellow mercuric oxide in 120 ml. of water was added slowly through a funnel 22.0 ml. (18.0 gm.) 1,2-dimethylhydrazine in 200 ml. of water. An additional 15 gm. of mercuric oxide was added and the reaction mixture was then stirred continuously at room temperature for two hours. On heating the reaction mixture, azomethane distilled over and was collected in two spiral traps cooled to -40°C. and -78°C. Yield: 17.0 ml. in the first trap and 0.5 ml. in the second. The azomethane was dried by slow distillation through a U-tube containing Drierite on a vacuum line. Yield: 12.7 gm. (74% Theor).

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## HYDROGEN PEROXIDE AND ITS ANALOGUES

### V. PHASE EQUILIBRIA IN THE SYSTEM $D_2O$ - $D_2O_2$ <sup>1</sup>

BY PAUL A. GIGUÈRE AND E. A. SECCO<sup>2</sup>

#### ABSTRACT

The cooling curves of a number of solutions of deuterium peroxide in heavy water in the concentration range 11% to 95% were measured in order to determine the solid-liquid phase diagram for that binary system. The apparatus of Herington and Handley, which uses a pulsing pressure for stirring the solutions, and a thermistor, was found to be particularly suitable for that purpose. As could be expected the freezing-point curve of the deuterated compounds is closely similar to that of the hydrogen compounds, being shifted up only by about 4° for water-rich solutions and by 2° for peroxide-rich solutions. The melting point of the addition compound,  $D_2O_2 \cdot 2D_2O$  very nearly coincides with one of the eutectic points at 46.2%  $D_2O_2$  and  $-51.5^\circ C$ ; the other eutectic point is at 60.5%  $D_2O_2$  and  $-55.1^\circ C$ . By extrapolation the melting point of pure deuterium peroxide is found to be  $1.5^\circ C$ , as compared with  $-0.43^\circ C$  for hydrogen peroxide. Concentrated solutions of deuterium peroxide exhibit an extreme tendency to supercool, resulting sometimes in formation of glasses even at liquid-air temperature. The previous results of Foley and Giguère for the system  $H_2O$ - $H_2O_2$  were confirmed, specially as regards the melting point of the addition compound  $H_2O_2 \cdot 2H_2O$ .

#### INTRODUCTION

For a simple molecule such as hydrogen peroxide substitution of hydrogen by deuterium may be expected to alter noticeably most of the physical properties, and particularly the melting point, by analogy with the case of water and heavy water. Direct determination of this property for the pure isotopic compound was not feasible because of the limited supply of starting material, heavy water, and the difficulty of obtaining an "anhydrous" product. Instead the method of thermal analysis was applied to a number of solutions of various concentrations which led to establishment of the phase diagram of the system  $D_2O$ - $D_2O_2$  and, by extrapolation, to the melting point of deuterium peroxide. Obviously this investigation was patterned after the well established phase diagram of the system  $H_2O$ - $H_2O_2$ .

#### EXPERIMENTAL

The thermometric method used previously in this laboratory (4) was followed but the precision freezing-point apparatus had to be modified because of the small samples available. The improved apparatus devised by Herington and Handley (13) turned out to be especially well adapted to the problem at hand. The major improvement rests in the manner of stirring the sample which allows the freezing curve to be followed until nearly complete solidification. This is achieved by placing the solution in a small U-tube and by applying a gentle pulsing pressure differential over one limb so that the liquid is rocked back and forth past the solid. In addition to a substantial reduction in the size of sample needed (only about 15 gm. was actually used) the new apparatus

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Contribution from the Department of Chemistry, Laval University, Quebec, Que. Presented at the XIIIth International Congress of Pure and Applied Chemistry in Stockholm, July 1953.

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has the further advantage of doing away with mechanical stirrers which would eventually catalyze the decomposition of the peroxide, thus leading to erroneous results.

As in the original apparatus of Herington and Handley the sensitive element was a thermistor (Western Electric, Type 14B) having a resistance of some 2000 ohms at 25°C.; the leads and terminal bead were inserted in a thin-walled glass tubing to avoid contact with the peroxide solution. The resistance was measured with a Wolff potentiometer - Wheatstone bridge combination, used in the latter fashion (23), and a Leeds and Northrup galvanometer with a sensitivity of 0.025  $\mu$  amp. per mm. The equation for the temperature coefficient of the thermistor (2)

$$[1] \quad \ln R/R_0 = (B/T - BT_0),$$

where  $R_0$  is the hypothetical resistance at °K., requires calibration at two points at least. Thus  $R$  was found to be 5874.7 ohms at the ice point, realized after the recommended method, and  $44,000 \pm 10$  ohms at  $-38.87^\circ\text{C.}$ , the melting point of mercury. The former datum was checked periodically against a set Beckmann thermometer.

The deuterium peroxide was prepared by dissociation of heavy water in the electrodeless discharge as described elsewhere (12). Some 175 gm. of 99.7% pure heavy water yielded about 130 gm. of a 50% solution of deuterium peroxide. By fractional distillation under reduced pressure this was separated roughly into three portions as follows: 50 gm. of 11%, 50 gm. of 47%, and 30 gm. of 96%  $\text{D}_2\text{O}_2$ . Solutions of various intermediate concentrations were prepared by mixing suitable proportions of these three samples; dilution with heavy water was avoided since it could yield an unstable solution, as was found in the case of hydrogen peroxide (8). The peroxide content was determined by duplicate titrations with 0.1  $N$  potassium permanganate using a microburette and fairly small samples (equivalent to 0.1 gm. of  $\text{D}_2\text{O}_2$ ); refractive index measurements (7,20) also served as a first indication. Because of the hygroscopic nature of concentrated peroxide solutions great care was necessary to prevent contamination of the samples by atmospheric moisture during the experiments. Thus the air used in the "pulsing meter" was dried over magnesium perchlorate. A check of the samples by means of infrared spectroscopy after the investigation was completed indicated no significant increase in the original content of ordinary hydrogen.

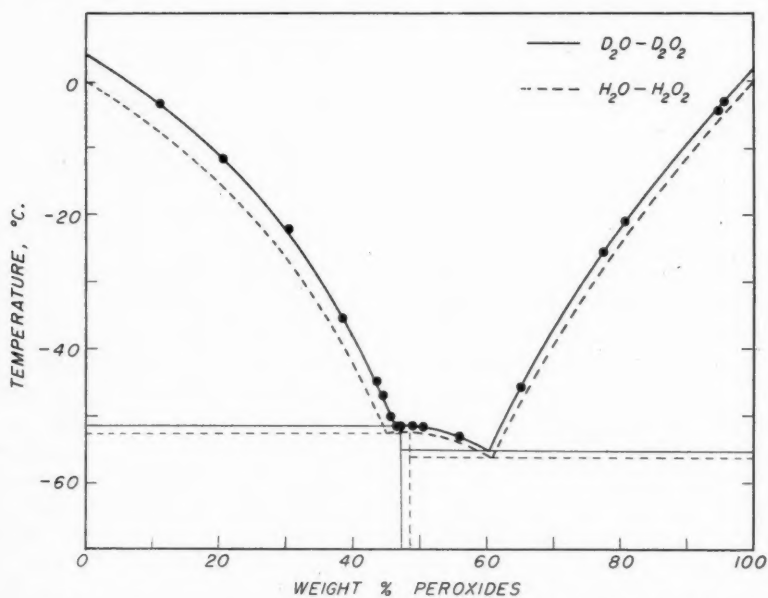
#### DISCUSSION OF RESULTS

The cooling curves for each mixture were drawn from temperature readings taken every minute at the beginning of solidification, and less frequently thereafter. It was always necessary to overcome supercooling by seeding the liquid with a few crystals made from the same mixture completely frozen in dry ice or liquid air. Duplicate determinations were carried out and the melting points, as found by the usual extrapolation method, agreed generally within  $0.01^\circ\text{C.}$  except in the region of the eutectics where the very high viscosity of the mixtures prevented reaching thermal equilibrium in reasonable time.

TABLE I  
 FREEZING POINTS FOR THE SYSTEM  $D_2O-D_2O_2$ 

Experiment No.	Weight % $D_2O_2$	Freezing point, °C.	Eutectic, °C.
	0.00	+ 3.80	
20	11.00	- 3.3 <sub>9</sub>	
5	20.6 <sub>2</sub>	-11.6 <sub>2</sub>	
9	30.4 <sub>6</sub>	-22.3 <sub>4</sub>	
8	38.5 <sub>1</sub>	-35.4 <sub>1</sub>	
10	43.5 <sub>1</sub>	-45.0 <sub>0</sub>	
11	44.6 <sub>8</sub>	-47.0 <sub>0</sub>	-51.3 <sub>7</sub>
12	45.8 <sub>4</sub>	-50.1 <sub>0</sub>	-51.3 <sub>2</sub>
17	46.5 <sub>1</sub>	-51.5 <sub>2</sub>	
7	46.9 <sub>6</sub>	-51.6 <sub>2</sub>	
14	48.8 <sub>4</sub>	-51.5 <sub>3</sub>	
13	50.3 <sub>5</sub>	-51.6 <sub>4</sub>	
15	56.0 <sub>5</sub>	-53.2 <sub>8</sub>	-55.1 <sub>0</sub>
22	61.1 <sub>7</sub>	—	-55.0 <sub>6</sub>
19	66.5 <sub>6</sub>	-43.7 <sub>6</sub>	
18	77.5 <sub>4</sub>	-25.8 <sub>1</sub>	
2	80.8 <sub>5</sub>	-20.9 <sub>6</sub>	
1	95.0	- 4.3 <sub>4</sub>	
3	95.8 <sub>5</sub>	- 3.0 <sub>7</sub>	

The various experiments were scattered according to the sequence shown in Table I in order to offset a possible drift in the characteristics of the thermistor, although frequent tests failed to give any such indication. In a few cases it was possible to detect the eutectic halt, and the temperatures thus observed con-


 FIG. 1. Phase diagram of the two binary systems  $D_2O-D_2O_2$  and  $H_2O-H_2O_2$ .

firmed exactly those found by graphic extrapolation of the three portions of the freezing-point curve. As may be seen in Fig. 1 these curves for the system of deuterium compounds are nearly parallel to those for the hydrogen compounds. For the water-rich mixtures the curve is shifted upwards by about 4°C. whereas for the peroxide-rich mixtures the shift is only half as large. Considering that these temperature differences are the same as between the melting points of the respective pure components the situation is in harmony with the absence of solid solutions in these binary systems as demonstrated otherwise (4, 9, 18).

On the other hand the melting point of the addition compound  $D_2O_2 \cdot 2D_2O$ ,  $-51.5^\circ C.$ , is only  $0.6^\circ C.$  above that of its hydrogen analogue (4), which may indicate a slightly decreased stability due to isotopic substitution. At any rate both compounds are quite unstable as shown by the very flat maximum of their curve.

Incidentally the present investigation confirms the results of Foley and Giguère (4) for the melting point of the compound  $H_2O_2 \cdot 2H_2O$ ,  $-52.1^\circ C.$  Their value is some  $2^\circ C.$  lower than that of most previous determinations (10, 15, 17, 18). If the higher value were correct, then the freezing-point curve for the hydrogen system of compounds would cross that for the deuterated compounds, which seems very unlikely *a priori*. As a further check a series of measurements on hydrogen peroxide solutions in the middle range of composition were made using the same apparatus as above. The results (Table II) are in complete agreement with those of Foley and Giguère, and furthermore, they allow a more accurate location of the eutectics (Table III). In particular the failure to observe both the freezing point and the eutectic halt in the same cooling curve for solutions in the concentrations range 45–48.6%  $H_2O_2$  is easily understood in view of the narrow gap,  $0.2^\circ C.$ , between these two temperatures.

TABLE II  
FREEZING POINTS OF SOME  $H_2O$ - $H_2O_2$  SOLUTIONS

Weight % $H_2O_2$	Freezing point, $^\circ C.$	Eutectic, $^\circ C.$
42.3 <sub>1</sub>	-46.2	-52.2
47.4 <sub>5</sub>	-51.9 <sub>6</sub>	
48.6 <sub>2</sub>	-51.9 <sub>9</sub>	
49.8 <sub>4</sub>	-52.0 <sub>2</sub>	
52.5 <sub>8</sub>	-52.5 <sub>1</sub>	-56.0
55.7 <sub>6</sub>	-53.4 <sub>1</sub>	-56.0
66.7 <sub>3</sub> (?)	-45.6 <sub>0</sub>	-56.1
73.8 <sub>4</sub>	-34.0 <sub>0</sub>	
76.4 <sub>9</sub>	-29.2 <sub>9</sub>	
98.7 <sub>6</sub>	-1.62	

Replacement of hydrogen by deuterium reduces still further the narrow range of the freezing-point curve of the addition compound because of greater overlapping by the two other curves (Fig. 1). This brings one of the eutectics almost in coincidence with the melting point of the compound  $D_2O_2 \cdot 2D_2O$ . (The composition difference is only of the order of 1%  $D_2O_2$  and no tempera-

TABLE III  
 COMPOUNDS AND EUTECTICS IN THE  $\text{H}_2\text{O}-\text{H}_2\text{O}_2$  AND  $\text{D}_2\text{O}-\text{D}_2\text{O}_2$  SYSTEMS

Weight % $\text{H}_2\text{O}_2$	Temp., °C.	Weight % $\text{D}_2\text{O}_2$	Temp., °C.	
45.2	-52.2	46.2	-51.5	Higher eutectic
48.55	-52.0	47.35	-51.5	Compound
61.2	-56.1	60.5	-55.1	Lower eutectic

ture difference could be detected experimentally.) By extrapolation from a large plot the melting point of pure deuterium peroxide was found to be  $1.5^\circ\text{C}$ . as compared with  $-0.43^\circ$  for  $\text{H}_2\text{O}_2^*$ . That the isotope effect on the melting point in the case of peroxide is exactly half that in the case of water ( $3.82^\circ\text{C}$ .) seems quite plausible considering that, (a) the molecular mass of the former is nearly double that of the latter and, (b) the difference in the zero-point energies of hydrogen and deuterium peroxides is of the same magnitude as that of water and heavy water (21).

Such notable differences in melting points due to substitution of deuterium for hydrogen—a mass increase of merely 6 or 10%—are in contrast with the surprising fact that hydrogen peroxide has nearly the same melting point as water ice despite a much greater relative mass. Now, melting-point relationships are based on considerations of two different kinds: first, the cohesion energy of the lattice and second, the symmetry of the individual molecules. In both water and hydrogen peroxide crystals packing is realized mainly through hydrogen bonds (1), each type of molecule forming the same number of such bonds with its nearest neighbors. From the heat of sublimation of the two solids, 12.2 and 15.6 kcal./mole (5,11) their hydrogen bond energies are found to be of the same magnitude, namely 4.5 (19) and 5.0 kcal./mole. Again comparison of their electric dipole moments 1.84 and 2.16 D and their polarizabilities, 1.48 and  $2.31 \times 10^{-24} \text{ cm}^3$  (6) shows that their lattice energies cannot be very different. Therefore both compounds are in comparable situations on that account, and their heats of fusion, 1435 and 2987 cal./mole, (9) are roughly in the ratio of their molecular masses as normally expected.

On the other hand, the water molecule, because of its higher symmetry, has fewer possible different orientations on melting and, consequently, its entropy of fusion is only half that of hydrogen peroxide. Furthermore, the constitution of the water molecule is such that it results in an unusually regular and well-balanced structure of the crystal. Although rather open, this structure is so stable that it persists to some extent even after melting. No such anomalies are to be found in hydrogen peroxide. Judging from their respective heat of fusion it appears that twice as many hydrogen bonds are broken on melting in hydrogen peroxide as in water ice (19). Obviously the same considerations apply to the deuterium compounds. So far the indications are that,

\*This value from recent very accurate calorimetric measurements (9) is considered more reliable than the thermometric result of Foley and Giguère,  $-0.46^\circ\text{C}$ . (4). The cause of the discrepancy is now evident, namely, the presence of about 0.03 mole % impurity (water) in the purest sample used by the latter authors. Because of poor thermal equilibrium in their freezing-point apparatus due to inadequate stirring, their calculated freezing points at zero impurity were erratic.

*ceteris paribus*, the energy of the deuterium bond is very slightly greater than that of the hydrogen bond (3, 16, 22).

The natural tendency of hydrogen peroxide solutions to supercool was found to be increased further by isotopic substitution. In some cases it became extremely difficult to obtain crystals for seeding the liquid in freezing-point determinations. Concentrated solutions, in particular, could be supercooled not only in dry ice but even in liquid air where they formed glassy transparent solids. Crystallization of these glasses took place only after some time (about 10 min.) and, in one instance, was so sudden that the test tube was shattered and the sample (5 gm. of 77.5%  $D_2O_2$ ) was lost. It is not clear, at present, why this tendency to supercool should be more pronounced in deuterium peroxide solutions. The increased viscosity of these solutions (20) may be responsible for the very slow rate of crystallization. As in the  $H_2O-H_2O_2$  system it was possible to supercool solutions of deuterium peroxide below the eutectic points even in presence of the "normal" solid phase (8). Dilute solutions of the isotopic peroxide in heavy water follow Raoult's law to the same extent as their hydrogen analogues (5); for instance at 3 mole %  $D_2O_2$  the freezing point lowering is calculated to be  $3.0^\circ C$ . whereas the experimental curve gives  $3.4^\circ$ . No measurement of the heat of fusion of deuterium peroxide has been made yet but a value of about 3030 cal./mole seems reasonable in comparison with the case of water and heavy water (14).

#### ACKNOWLEDGMENT

The authors are indebted to The Consolidated Mining and Smelting Co. for a postgraduate Cominco Fellowship, and to the National Research Council of Canada for a research grant.

#### RÉSUMÉ

On a déterminé par analyse thermique le diagramme des phases du système  $D_2O-D_2O_2$ . Comme on pouvait le prévoir la courbe des points de fusion suit de près celle du système analogue  $H_2O-H_2O_2$ ; la substitution isotopique élève le point de fusion des solutions diluées de peroxyde d'environ  $4^\circ C$ . tandis que pour les solutions concentrées l'effet est la moitié moindre. Par extrapolation on arrive à un point de fusion de  $1.5^\circ C$ . pour le peroxyde de deutérium pur. L'un des eutectiques, à 46.2% de  $D_2O_2$  et  $-51.5^\circ C$ ., se confond presque exactement avec le point de fusion du composé moléculaire  $D_2O_2 \cdot 2D_2O$ ; l'autre se trouve à 60.5% de  $D_2O_2$  et  $-55.1^\circ C$ . La tendance à la surfusion est encore plus marquée chez les solutions de peroxyde isotopique que chez celles de peroxyde d'hydrogène.

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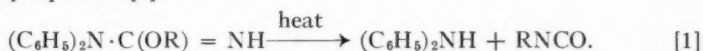


## NOTES

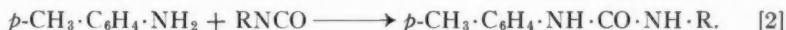
### THE PRODUCTION OF ISOCYANATES BY THE THERMAL DECOMPOSITION OF PSEUDOUREAS

BY J. R. ROBINSON\*

In studies involving an homologous series of 3,3-diphenyl-2-alkylpseudo-ureas the materials were observed to decompose when distillation was attempted at atmospheric pressure. One of the decomposition products was the corresponding alkyl isocyanate and the other major product was diphenylamine, as indicated by equation [1].

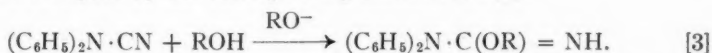


The isocyanates distilled over at 250–300°C. and were converted to 1-alkyl-3-*p*-tolylureas by treatment with *p*-toluidine [2] to facilitate identification.



The low yields of substituted urea (Table I) indicate correspondingly low yields of isocyanate, and were probably due to polymerization and recombination processes. No precautions were taken to minimize these side reactions.

The pseudoureas were synthesized by the addition of alcohols to diphenylcyanamide, catalyzed by the corresponding alkoxide ion [3].



The pyrolysis of the methyl homologue has been described elsewhere (3) as producing unsymmetrical diphenylurea. That process occurs when the temperature is kept below 160°C.

### EXPERIMENTAL

In each case, 1 to 3 gm. (0.005 to 0.01 mole) of the pseudourea was weighed into a 6 in. soft glass test tube which was then drawn off to a fine delivery tube and bent around to form a semimicro retort. The melting and subsequent thermal decomposition of the material were performed as slowly and at as low a temperature as possible, usually at 250–300°C. The lachrymatory distillate was collected in a cooled 10 ml. Erlenmeyer flask and the pyrolysis was stopped when diphenylamine began to distill over. The crude isocyanate was mixed immediately with the theoretically required amount of *p*-toluidine dissolved in 10 ml. of diethyl ether. The resulting solution was left standing in an ice-water bath until crystallization of the substituted urea was complete. The product was crystallized from methanol-water, ethanol-water, and finally from petroleum ether (65–110°), then dried for seven days in a vacuum desiccator containing calcium chloride and shredded paraffin wax.

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The yields and analytical data for the 1-alkyl-3-*p*-tolylureas are shown in Table I.

TABLE I  
1-ALKYL-3-*p*-TOLYLUREAS.  $p\text{-CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{R}$

R	Yield,* %	M.p., °C.	M.p. in lit.	Lit. ref.	Calc., %		Found, %**	
					C	H	C	H
Methyl	12	178	178	(1)	65.8	7.37	65.7	7.47
Ethyl	30	143	144	(2)	67.4	7.92	67.6	7.99
<i>n</i> -Propyl	21	125	123	(1)	68.7	8.39	68.7	8.32
Isopropyl	10	157	157	(1)	68.7	8.39	68.9	8.48
<i>n</i> -Butyl	21	119	119	(1)	69.9	8.80	70.0	8.74
Isobutyl	15	153	154	(1)	69.9	8.80	70.0	8.91
<i>n</i> -Amyl	6	103	—	—	70.9	9.15	70.9	9.22
<i>n</i> -Hexyl	11	86	—	—	71.8	9.46	71.7	9.46
<i>n</i> -Heptyl	10	108	—	—	72.5	9.74	72.7	10.03
<i>n</i> -Octyl	6	92	—	—	73.2	9.99	73.6	9.90
<i>n</i> -Nonyl	11	99	—	—	73.9	10.21	73.9	10.32
<i>n</i> -Decyl	3	98	—	—	74.4	10.41	74.6	10.27
<i>n</i> -Undecyl	8	102	—	—	75.0	10.59	74.9	10.68
Lauryl	1	102	—	—	75.4	10.76	75.4	10.70

\*Yields calculated after three crystallizations.

\*\*Combustion analyses by Mr. R. W. White of the Science Service Laboratory, Department of Agriculture, London, Ont.

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## THE ADSORPTION OF WATER VAPOR BY PROTEINS

By H. B. DUNFORD AND JOHN L. MORRISON

Bull (3) measured the adsorption of water vapor by a large number of proteins and found that the Brunauer-Emmett-Teller equation (2) fitted the isotherms for the range of relative vapor pressures 0.05 to 0.5. This observation led him to suggest that the water was specifically adsorbed by polar groups in the protein molecule. The B.E.T. surface area measurements indicate that proteins present a large internal surface to water which is not accessible to relatively inert gases such as nitrogen and oxygen (1).

Less is known about the water sorption process at relative pressures greater than 0.5, where the two-constant B.E.T. equation is not applicable. However, solution effects (3) and a spectrum of sorption processes (4) have been postulated.

This note reports the application of the Harkins-Jura equation (5) to Bull's water-protein adsorption isotherms. Some examples of the plotting are given

in Fig. 1. Linear H.J. plots for most of Bull's data are obtained over the relative water vapor pressure range from 0.5 or 0.6 to 0.95. The notable exception is salmin. Salmin, which is not a true protein but a low molecular weight polypeptide, goes into solution at a relative vapor pressure of 0.7 (3). The nylon isotherms yield linear H.J. plots over the shorter range of 0.7 to 0.95.

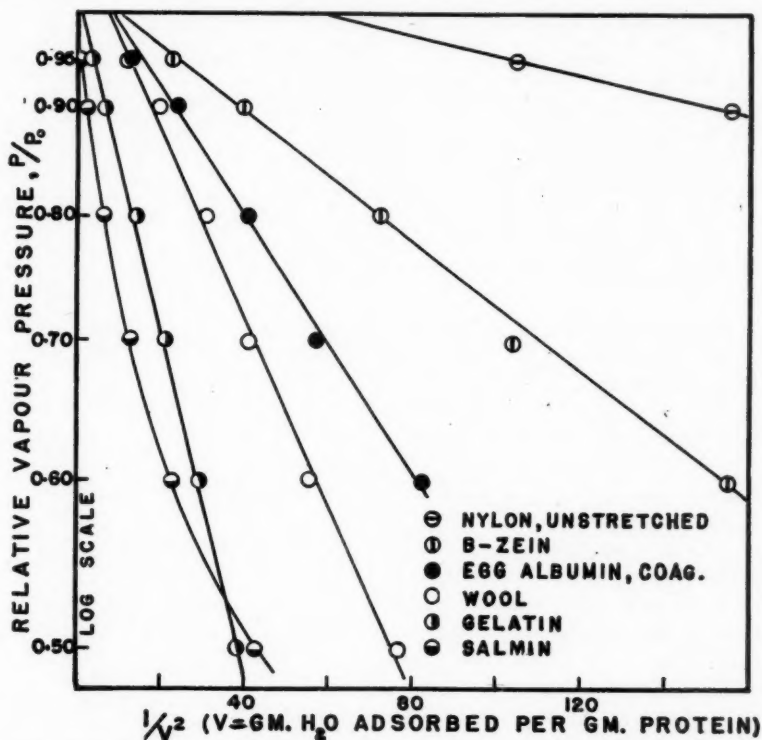


FIG. 1. Harkins-Jura plots of some of Bull's water-protein adsorption isotherms at 25°C.

Liang's method (6) was used to correlate the results of the two equations. Liang has shown that the slope of a linear H.J. plot is related to  $V_m$ , the amount in a monomolecular layer as given by the B.E.T. equation. Table I contains the  $V_m$  values calculated from the H.J. equation as well as those obtained by Bull from the B.E.T. equation. With the exception of salmin, the values agree with a 5% mean deviation.

The Harkins-Jura equation is based on the assumption that the adsorbed molecules are in a condensed film. Thus it is probable that the adsorption of a condensed film of water by proteins is the predominant process at high vapor pressures.

The general observation that the same  $V_m$  is obtained for the upper and lower parts of the isotherms may be explained by one of two possible alternatives.

TABLE I  
 GRAMS WATER IN MONOLAYER PER 100 GRAMS PROTEIN

Protein	B.E.T. equation (ref. 3)	H.J. equation
Nylon, unstretched	1.92	2.11
Nylon, stretched	1.76	2.02
Silk	4.07	4.11
Wool	6.58	6.26
B-zein	4.10	3.89
C-zein	3.78	4.00
Salmin	5.28	—
Elastin	6.22	6.81
Collagen	9.52	10.4
Gelatin	8.73	8.77
Egg albumin, lyophilized	5.65	5.54
Egg albumin, unlyophilized	6.15	6.09
Egg albumin, heat coagulated	4.97	5.50
$\beta$ -Lactoglobulin, lyophilized	5.93	6.11
$\beta$ -Lactoglobulin, wet crystals	6.67	6.48
Serum albumin	6.73	6.48
$\alpha$ - and $\beta$ -Pseudoglobulin	7.15	7.00
$\gamma$ -Pseudoglobulin	7.16	7.00

The alternatives are that the complete isotherm represents *either* the formation of a film of one molecule thickness which becomes condensed at higher vapor pressures *or* the formation of a film of at least two molecules thickness, the upper layer being condensed and occupying the same surface area as the underlying monomolecular layer. The concurrence of the  $V_m$  values for the two parts of the isotherm means that the same number of adsorption sites are involved. This, together with the observation that in all cases an amount of water greater than  $V_m$  is adsorbed well before a relative vapor pressure of 0.5 is reached (3), suggests that the second alternative is the correct one.

The fact that nylon obeys the H.J. equation over a shorter pressure range than the other proteins may be due to the large water-repellant hydrocarbon spacings between the peptide linkages of the synthetic polypeptide hindering condensed film formation.

The concurrence of the  $V_m$  values given by the B.E.T. and H.J. equations for the two separate halves of the water-protein adsorption isotherms suggests an interesting extension of Liang's method.

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